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LONDON: GURNEY AND JACKSON
33, PATERNOSTER ROW, E.C. 4

Printed in Great Britain by Richard Clay & Sons, Ltd.,
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The annual subscription is £3. Those desiring to become Fellows of the Society should apply for further information to the Secretaries, Burlington House, London, W. 1.

The suggestion has been made (Bailey, *loc. cit.*) that the disappearance of colour in the dark or on heating can be explained in one of two ways. An equilibrium may exist between tautomeric forms of thiocyanic acid, of which the colourless form alone is stable at high temperatures and in the dark, or else a coloured complex, dissociated by heat or in the dark, is formed between the acid and the oxygen-containing solvent. The existence of a compound composed of equal numbers of molecules of thiocyanic acid and ether has been noted by Klason (*J. pr. Chem.*, 1887, **35**, 400). The possibility that the pink colour may be due to traces of iron cannot be ruled out, as is clear from the results obtained by Parenti (*Gazzetta*, 1889, **19**, 175) on repeating the earlier work of Miquel (*Bull. Soc. chim.*, 1876, **26**, 442). This point is being investigated.—TRINITY COLLEGE, DUBLIN. [*Received, September 10th*, 1926.]

The Condensation of Quinaldine with m-*Nitrobenzaldehyde.* By THOMAS WESTON JOHNS TAYLOR and CHARLES POWYS WOODHOUSE.

IF quinaldine and *m*-nitrobenzaldehyde are condensed together by heating on the water-bath either with or without addition of zinc chloride, the sole product is 2-*m*-nitrostyrylquinoline, which crystallises from alcohol in yellow needles, m. p. 156° (Found: C, 74·0; H, 4·65; N, 9·83; *M*, in nitrobenzene, 272·5; in ethylene dibromide, 289·7. Calc.: C, 73·9; H, 4·3; N, 10·1%; *M*, 276). The picrate melts at 261° (decomp.). The compound is unaffected by boiling with acetic anhydride.

The observations of Wartanian (*Ber.*, 1890, **23**, 3645) as to the physical properties of this compound and as to the simultaneous formation in the above condensation of 2-β-hydroxy-β-*m*-nitrophenylethylquinoline are incorrect.

The styryl compound unites with bromine in chloroform solution to give a dibromide, which can be recrystallised from alcohol; m. p. 170—171° (Found: Br, 36·4. Calc.: Br, 36·7%).—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, June 9th*, 1926.]

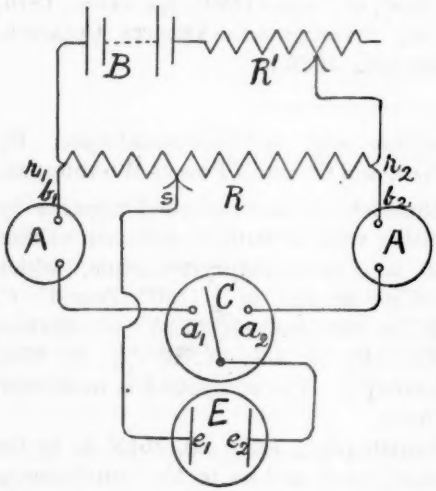
Arrangement for Alternating Current Electrolysis. By HENRY J. S. SAND and WILLIAM V. LLOYD.

EXPERIMENTS on superposing an alternating on a continuous current are often of considerable interest and importance (*e.g.*, Allmand and Barklie, *Trans. Faraday Soc.*, 1926, **22**, 35, which also gives further references). In many electrochemical laboratories the alternating current and the measuring instruments required for such experiments are not available. Moreover, it may be desirable

to measure electrode potentials separately during each pulse of the current, a possibility which, so far as we are aware, has hitherto not been realised (Glasstone, *J. Amer. Chem. Soc.*, 1925, **47**, 940).

We describe the following circuit in the hope that it may be as useful to others as it has been to ourselves. It makes use of a source of continuous current and a revolving three-point commutator. Successive alternating pulses of arbitrarily adjustable value may be obtained and separately measured. The ammeter may be a direct-current instrument. Thus all the electrolytic effects obtainable by superposing alternating on direct current may be produced, the sinusoidal character of the alternating current being of no importance in such experiments.

FIG. 1.



The accompanying figure is sufficiently explanatory. A suitable voltage can be impressed on the ends r_1 and r_2 of the sliding rheostat, R, by means of the battery, B, and the back resistance, R'. The slider s is connected to one of the electrodes e_1 of the cell E, the other electrode, e_2, being connected through the commutator, C, alternately *via* the points a_1, b_1 or a_2, b_2, respectively, to the two ends, r_1 and r_2, of the sliding rheostat. The branches $a_1 b_1$ and $a_2 b_2$ may each include an ammeter, A, but as a rule one ammeter suffices if it be successively interposed in either branch as required. (This can be easily arranged by means of a combined double-pole switch and short-circuiting key such as can be improvised from a Pohl commutator.) If two uni-directional pulses of different magnitude, corresponding to a feeble alternating current superposed on a more powerful continuous one, are required, they can be readily obtained by altering, say, the connexions e_1 s and b_2 r_2 into e_1 r_2 and b_2 s. By the use of suitably designed commutators, the time during which successive pulses are in operation may be made unequal.

Where electrode potentials during each pulse are to be measured, a second two-point revolving commutator is mounted on the same shaft as the first. The auxiliary electrode is best permanently connected to one terminal of the potentiometer, the working

electrode under examination being connected through the two-point commutator to the other terminal of the potentiometer. The construction of the two-point commutator should be such that connexion is only made during a slightly shorter interval than that during which the pulse to be examined flows through the cell. The well-known Whetham double commutator can be readily adapted to the purpose, three unnecessary brushes being removed.—SIR JOHN CASS TECHNICAL INSTITUTE, E.C. 3. [*Received, September 16th*, 1926.]

CCCXCVIII.—*The Diffusion of Zinc in the α-Series of Solid Solution in Copper.*

By JOHN STANLEY DUNN.

THE phenomenon of diffusion in solid substances presents many points of considerable interest, but the experimental difficulties encountered, *e.g.*, by Roberts Austen (Bakerian Lecture, 1896; *Proc. Roy. Soc.*, 1900, **67**, 101), van Ostrand and Dewey (U.S. Geol. Survey, 1915, Paper 95G), and von Hevesy (*Ann. Physik*, 1921, **65**, 218), have deterred investigators from making a thorough quantitative study of the process.

Several points connected with the phenomenon of diffusion require further elucidation. Von Hevesy (*Nature*, 1925, **115**, 674) and Geiss and van Liempt (*Z. Metallk.*, 1924, **16**, 316) claim to have shown that diffusion into single crystals does not occur. On the other hand, microscopic evidence indicates that diffusion takes place throughout the whole mass and not merely along the crystal boundaries. Von Hevesy suggested that the phenomena of diffusion and of electrolytic conductivity in crystals are due to the presence of loosened patches in the crystal lattice through which the atoms and ions may move with comparative ease. The author investigated this idea theoretically (*Proc. Roy. Soc.*, 1926, **111**, 203) and found that an expression of the type

$$D = Ae^{-Q/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

should describe the variation of the diffusion coefficient (and by a natural extension that of the conductivity) with temperature. (Here, D is the diffusion coefficient or conductivity, R and T have their usual significance, and A and Q are constants.) It has been shown that this equation describes with considerable accuracy the diffusion of oxygen through films of metallic oxide, and the data of Horton (*Phil. Mag.*, 1906, **11**, 505), Streintz ("Das Leitvermogen von Gepressten Pulvern"), Rasch and Hinrichsen (*Z. Elektrochem.*,

1908, **14**, 41), Konigsberger (*Physikal. Z.*, 1907, **8**, 883), and Phipps, Lansing, and Cooke (*J. Amer. Chem. Soc.*, 1926, **48**, 112) show a similar agreement for conductivity phenomena.

Although Dushman and Langmuir have claimed the validity of this equation for diffusion in solid metals, the published data upon this point might well be amplified, for the figures of Roberts Austen, on the one hand, and of van Ostrand and Dewey on the other, show considerable variation.

The objects of the present investigation were : (1) To work out a simpler technique for the investigation of diffusion phenomena; (2) to measure the diffusion coefficient in circumstances which admit of little doubt concerning the fact of diffusion within the crystal; and (3) to test the validity of equation (1) and, incidentally, of von Hevesy's theory of lattice loosening.

It has long been known that when brass is heated in an inert gas or in a vacuum it loses zinc in the form of vapour. Turner (*J. Inst. Metals*, 1912, **7**, 105) showed that the whole of the zinc might be removed from molten brass and, together with Thorneycroft (*ibid.*, 1914, **12**, 214), made a study of a series of the brasses when heated in a vacuum. It was not realised, however, that this phenomenon afforded a remarkably simple method for the study of the diffusion of zinc in solid brass.

If zinc is allowed to evaporate in a vacuum from a brass surface the process becomes analogous to a well-known physical process—the cooling of a semi-infinite solid under the conditions of initially uniform temperature and boundary conditions $T = 0$ for $t > 0$, t representing time. The problem is indeed identical with that investigated by Rayleigh in his estimation of the age of the earth from the temperature gradient at the surface. A somewhat similar method has been used by Langmuir to determine the diffusion coefficients of thorium in tungsten (*Physical Rev.*, October, 1923), but his mathematical treatment is more involved since his experimental conditions did not permit of the use of the semi-infinite solid as an approximation.

The solution of the diffusion equation under these conditions is

$$C = \frac{2C_0}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-u^2} du.$$

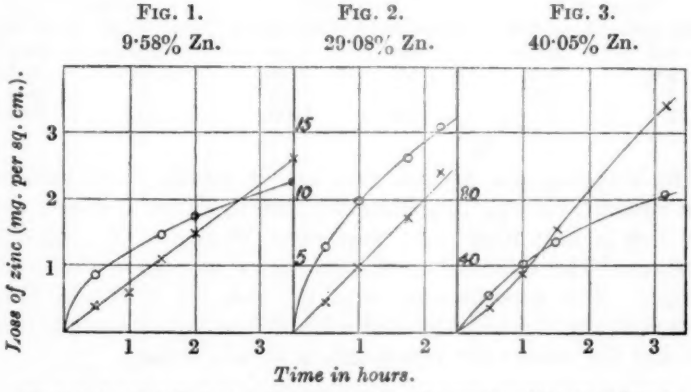
This expression may be integrated with the aid of tables, and we then know the concentration of zinc, C, at a distance x from the surface for an arbitrarily chosen value of D. Plotting concentration against distance, the total amount of zinc lost in a constant time, t, can be calculated by a graphic integration. It can be seen by inspection that the amount of zinc diffusing to the

surface and across is proportional to $\sqrt{Dt}$. If, therefore, an arbitrary value be assigned to D, the amount of zinc lost in a time t can be calculated, and the value of D which obtains for the specimen under examination is then found by simple proportion.

A numerical example will make this clear. For a value of $D = 1/360^2 = 0{\cdot}0_577$ by graphic integration we find that $9{\cdot}39 \times 2/\sqrt{\pi}\% = 10{\cdot}7\%$ of the total zinc is lost from 2 c.c. of brass across a surface of 1 sq. cm. in an hour. For a brass of d 8·86 containing 9·58% of zinc this corresponds with a loss of $(8{\cdot}86 \times 2 \times 10{\cdot}7/100) \times (9{\cdot}58/100) = 0{\cdot}1816$ g. $= 181{\cdot}6$ mg. At 842° the actual loss is 1·201 mg./sq. cm. Hence if D is the required diffusion coefficient,

$$\sqrt{0{\cdot}0000077} : \sqrt{D} = 181{\cdot}6 : 1{\cdot}201,$$

i.e., $$D = 3{\cdot}36 \times 10^{-12} \text{ cm.}^2 \text{ per second.}$$



(*Points denoted thus* × *represent squares of corresponding* ○ *values.*)

The experimental work entailed in such a determination occupies little more than an hour and the only observations necessary are two weighings.

The apparatus was comparatively simple. The specimen in the form of a helical coil of wire was placed in a silica tube sealed at one end and connected to a Töpler pump at the other. After exhaustion the closed end of the silica tube was placed in an electric furnace, the specimen resting on the other end which projected some inches from the furnace and remained cool. When thermal equilibrium had been established, the specimen was allowed to slide down to the hot end of the tube, the Töpler pump being kept in constant operation. At the end of the experiment the tube was withdrawn from the furnace and allowed to cool rapidly; the loss of zinc was then estimated by weighing.

The theory demands that the amount of zinc lost shall vary as

the square-root of the time, *i.e.*, $W = k\sqrt{t}$. This relationship is obeyed accurately for alloys containing up to 30% of zinc, but for an alloy containing 40% of zinc a departure is observed, too much zinc being lost over long time intervals.

The results obtained for the loss of zinc with time are shown in Table I, and are plotted in Figs. 1, 2, and 3. The circles represent zinc lost and the crosses the squares of this quantity. The conformity of the two specimens to the equation $W = k\sqrt{t}$ is shown by the fact that the crosses lie on a straight line passing through the origin.

TABLE I.

Rate of Loss of Zinc from a Brass Surface.

Comp. of brass: 90·42% Cu, 9·58% Zn. Temp. 842°.		Comp. of brass: 70·86% Cu, 29·08% Zn. Temp. 842°.		Comp. of brass: 59·90% Cu, 40·05% Zn. Temp. 775°.	
Time (hrs.).	Loss (mg.).	Time (hrs.).	Loss (mg.).	Time (hrs.).	Loss (mg.).
0·5	0·835	0·5	6·46	0·5	22·4
1·0	0·98	1·0	9·90	1·0	41·55
1·5	1·47	1·75	13·25	1·5	55·1
2·0	1·73	2·25	15·49	3·16	83·4
3·5	2·25				

The zinc loss per sq. cm. rose rather rapidly with increasing zinc content, obeying approximately the equation $L = ae^C$, where zinc lost in unit time $= L$; percentage of zinc $= C$; and a is a constant. The diffusion coefficient varies in a somewhat similar manner. The experimental data are set out in Table II and plotted in Fig. 4, where the circles denote the actual amounts of zinc lost and the crosses the logarithms of these numbers.

TABLE II.

The Influence of Composition upon the Rate of Loss of Zinc from a Brass Surface.

	Loss of zinc (in mg. per sq. cm.) in 30 mins.	
Zinc in alloy (%).	At 775°.	At 842°.
9·58	0·441	0·850
13·34	0·840	1·41
17·30	—	2·09
23·13	2·60, 2·85	4·60
29·08	2·76, 2·83	6·47
40·05	18·8	58·0

Both the rate of zinc loss and the diffusion coefficient vary exponentially with temperature, a result foreshadowed by the author's work upon diffusion of gases through solid oxide films and that of Langmuir and Dushman on metallic diffusion.

The experimental values are in Table III. On plotting the logarithm of the diffusion coefficient against the reciprocal of the

absolute temperature (Fig. 5), a fairly straight line is obtained for the 29%-zinc alloy and an excellent one for the 9·5% alloy, thus establishing equation (1).

TABLE III.

Temp.	Loss of zinc (mg. per sq. cm.) in 30 mins.	$10^{12} \times D$. (cm.²/per sec.).	Loss of zinc (mg. per sq. cm.) in 30 mins.	$10^{12} \times D$. (cm.²/per sec.).
	Alloy containing 9·58% Zn.		Alloy containing 29·08% Zn.	
641°	0·104	0·0507	0·649, 0·667	0·226
725	0·296	0·409	1·73	1·62
775	0·441	0·910	2·76, 2·83	4·10, 4·32
842	0·850	3·36	6·47	22·6
884	1·165	6·33	7·87	33·6

FIG. 4.

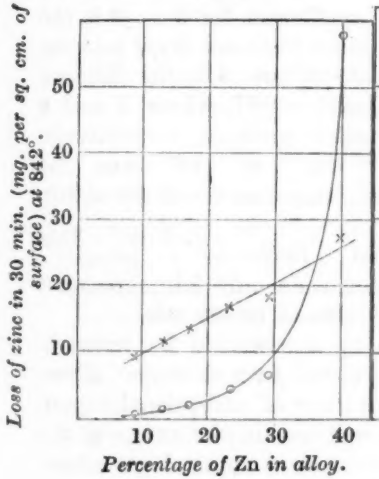
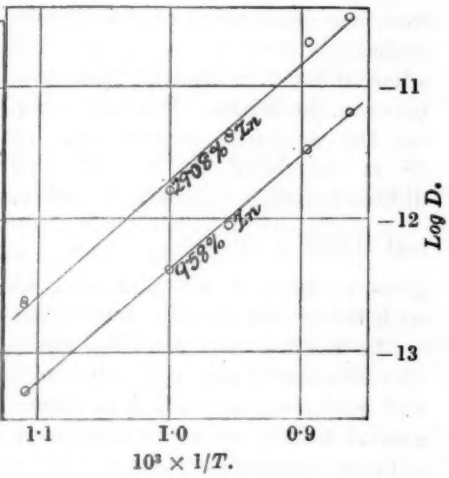


FIG. 5.



Discussion.

The form of the zinc loss–time curves calls for little discussion in the case of alloys containing up to 30% zinc. They are quadratic parabolas as demanded by theory and justify the use of this method for the study of diffusion in solid solutions.

The case of the alloy containing 40% of zinc is anomalous and may be complicated by the fact that during the course of diffusion the interior of the brass consists of the β-constituent, whilst the surface layers are composed of the α-brass only. A more detailed study of a 40%-zinc alloy is projected.

The possible diffusion of copper into brass has been ignored in the foregoing considerations. This is probably of minor importance for small losses of zinc, but when these reach the magnitude observed

in the 40%-zinc alloys it is no longer safe to neglect it, and the departure of these alloys from the parabolic law may be due in some measure to this factor of which the intervention would cause a departure from the ideal law in the same sense as that actually observed.

The rapid rise of the rate of zinc evolution and the diffusion coefficient with increasing zinc content is remarkable and indicates that the solid solution of zinc in copper deviates very considerably from ideal conditions. The square of the rate of zinc loss or the diffusion coefficient may be taken as a measure of the activity or thermodynamic concentration of the zinc in solid solution.

According to the equation proposed by Rideal and Dushman (*J. Amer. Chem. Soc.*, 1921, **43**, 397; *Physical Rev.*, 1922, **20**, 113), it should be possible to calculate the value of Q in equation (1) from one observation of the diffusion coefficient, for if $\kappa \,.\, dt$ is the probability that an atom of zinc will move from one layer into the adjacent layer in time dt, then $D = \kappa S^2$, where S is the distance between the layers. Further, $\kappa = (Q/Nh) \,.\, e^{-Q/RT}$, where N and h are the Avogadro number and Planck's constant, respectively. S^2 is calculated to be $5{\cdot}23 \times 10^{-16}$ cm.; at 1157° Abs. the diffusion coefficient is $6{\cdot}35 \times 10^{-12}$ cm.; therefore $\kappa = 1{\cdot}209 \times 10^4$, and $1{\cdot}209 \times 10^4 = \dfrac{Q}{6{\cdot}06 \times 10^{23} \times 6{\cdot}55 \times 10^{-27}} \,.\, e^{-\frac{Q}{1{\cdot}98 \times 1157}}$. This gives by trial, $Q = 12{,}800$ cals., which is in only fair agreement with the experimentally determined value of 10,750 cals.

The method now described opens up a new field for research. The diffusion of zinc and cadmium in metals such as copper, silver, and gold may be studied in circumstances of exceptional experimental facility up to temperatures well within the range of the ordinary resistance furnace. By working at much higher temperatures, Langmuir has shown it to be possible to evaporate a number of metals from electrically-heated tungsten and molybdenum alloys, and a complete survey of this field would undoubtedly be of great theoretical interest. The method may be applied to single crystals of zinc and cadmium alloys as soon as these have been produced and may then, with the aid of the microscope and suitable etching reagents, be used for a study of the directional diffusive properties of metallic crystals.

Summary.

The loss of zinc from a heated brass surface in a vacuum has been studied with reference to the influence of temperature, time, and composition.

It has been shown that measurements of the diffusion coefficient

of zinc in the α-ranges of solid solution in copper can readily be made by observing the rate of loss of zinc.

The diffusion coefficient has been shown to vary exponentially with zinc content and with temperature.

The temperature coefficient of diffusion has been shown to be in fair agreement with the Rideal–Dushman unimolecular reaction equation.

The possibility of using this method for a general survey of the question of diffusion in solid solution has been emphasised.

The author wishes to thank the Council of the British Non-Ferrous Metals Research Association for permission to publish this work.

THE LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE. [*Received, July 10th*, 1926.]

CCCXCIX.—*The Crotonic Acid Series. Part I. Nitrogen Derivatives of Crotonic Acid.*

By MONTAGUE ALEXANDRA PHILLIPS.

THE great difference in the rates of hydrolysis by aqueous sodium hydroxide of the isomeric α-ethylcrotonamides has been demonstrated by Newbery (J., 1925, **127**, 295). This author also showed the relationships existing between the carbamides and amides of the α-ethylcrotonic acids, and there is little doubt that the carbamide, m. p. 198°, and the amide, m. p. 104°, are labile forms, and the carbamide, m. p. 158°, and amide, m. p. 118°, the corresponding stable forms.

It was thought worth while to extend this investigation to the simplest member of the series which can display *cis–trans* isomerism, and the present paper deals with some nitrogen derivatives of crotonic acid.

Crotonic acid is known in a stable (m. p. 72°, b. p. 189°) and a labile (m. p. 15°, b. p. 169°) form. Two amides have been described. One of these, the labile form, m. p. 102°, is obtained from the other, the stable isomeride, m. p. 158°, by the action of ultra-violet radiation (Stoermer and Roberts, *Ber.*, 1922, **55**, 1030). By no simple chemical means, however, has the author been able to obtain any form of the amide other than that melting at 158°. This amide, on hydrolysis by caustic alkali, is quantitatively converted into the stable crotonic acid, m. p. 72°.

Two *carbamides* have now been prepared. One, m. p. 207°, was obtained from α-bromobutyrylcarbamide by the action of aqueous sodium hydroxide (1 mol.), and on hydrolysis even with one mole-

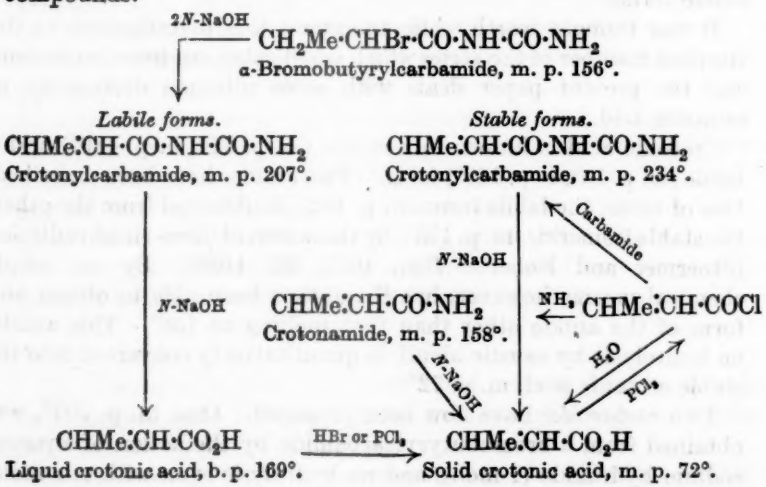
cular proportion of sodium hydroxide gave a mixture of *cis*- and *trans*-crotonic acids which did not solidify at 0°. This mixture was readily and quantitatively converted into the *trans*-acid, m. p. 72°, by the action of phosphorus trichloride followed by water at the ordinary temperature, or by a trace of hydrobromic acid. The carbamide of m. p. 207° is therefore the labile or *cis*-form.

The isomeric *carbamide*, m. p. 234°, was obtained by the action of carbamide on crotonyl chloride (made by the action of phosphorus trichloride on the *cis*-acid, the *trans*-acid, or a mixture of the two). It gave a quantitative yield of crotonic acid, m. p. 72°, on treatment with one molecular proportion of sodium hydroxide and is therefore the stable or *trans*-form.

Both carbamides gave *n*-butyric acid on reduction with sodium and alcohol; and from both, on hydrolysis, carbamide was produced, but no trace of amide. The lower-melting carbamide decomposed on treatment with hydrobromic acid and therefore could not thus be converted into the isomeride.

The stability of the crotonamide, m. p. 158°, is evidently of a very different order from that of the α-ethylcrotonamides described by Newbery (*loc. cit.*), as might have been expected owing to the removal of the protecting ethyl group in the α-position. A direct comparison of the rates of hydrolysis confirmed this view, for on heating crotonamide, m. p. 158°, with *N*-caustic alkali at 80° for 30 minutes a quantitative yield of crotonic acid, m. p. 72°, was obtained. Similar treatment of the α-ethylcrotonamides left the materials largely unchanged.

A scheme is given showing the relationships between the preceding compounds.



EXPERIMENTAL.

α-Bromobutyrylcarbamide.—α-Bromobutyryl bromide (b. p. 100—110°/100 mm.) was prepared in 80% yield from commercial butyric acid by the Hell–Volhard–Zelinski method (*Ber.*, 1887, **20**, 2026).

A mixture of 14 g. of dry carbamide with 21·7 g. of α-bromobutyryl bromide was kept at 60° for 15—20 minutes, 100 c.c. of water were then added and the mixture was heated on the water-bath to decompose the sticky mass. After being washed with water and recrystallised from alcohol, the *carbamide* had m. p. 156° (Found: N, 13·5; Br, 38·4. $C_5H_9O_2N_2Br$ requires N, 13·4; Br, 38·2%).

trans-Crotonic acid was prepared in 40—50% yield from malonic acid and acetaldehyde by the method of Schiebler and Magasanik (*Ber.*, 1915, **48**, 1810). An alternative method, giving a 70—80% yield of the mixed isomerides, was treatment of α-bromobutyryl bromide with alcoholic potassium hydroxide (1 mol.) followed by acidification and ether-extraction.

Crotonyl chloride, b. p. 124—127°, was prepared in 70% yield by treating 43 g. of the *trans*-acid (or the *cis–trans*-mixture) with 25 g. of phosphorus trichloride, decanting the upper layer after 3—4 hours, and distilling it.

Crotonamide (4 g.) was obtained by dropping 10 g. of crotonyl chloride slowly into 15 c.c. of cooled ammonia (*d* 0·880). After being washed and crystallised from benzene, it melted at 158° (Found: N, 16·3. Calc.: N, 16·5%).

Crotonylcarbamide, m. p. 234°.—A mixture of 16 g. of crotonyl chloride and 20 g. of dry carbamide was kept at 70° for 30 minutes, 100 c.c. of water were then added, and the mixture was heated on the water-bath until the sticky mass had decomposed (15—20 minutes). After cooling, the crystalline mass was filtered off, washed, and recrystallised from alcohol. The yield varied from 40—60% of the theoretical (Found: C, 46·5; H, 6·4; N, 22·1, 22·0. $C_5H_8O_2N_2$ requires C, 46·8; H, 6·25; N, 21·9%).

Crotonylcarbamide, m. p. 234°, is not appreciably soluble in water or alcohol, and does not decolorise bromine water in the cold, behaving in this respect like the α-ethylcrotonylcarbamides (Newbery, *loc. cit.*).

Crotonylcarbamide, m. p. 207°.—α-Bromobutyrylcarbamide (55 g.) was heated on the steam-bath with a solution of 11 g. of sodium hydroxide in 135 c.c. of water. Ammonia was evolved at once, and after 15 minutes the solution became acid to litmus. The heating was continued for 10 minutes, the solution then made alkaline with 2*N*-sodium hydroxide, excess of sodium chloride added, and the crystalline precipitate filtered off (*a*). The filtrate was exhaust-

ively extracted with (*b*) chloroform and (*c*) ether. The aqueous residue was made acid to Congo-red, and exhaustively extracted with ether (*d*).

After recrystallisation from alcohol, the solid (*a*) weighed 10 g., had m. p. 207°, and was the isomeric *crotonylcarbamide* (Found: C, 46·6; H, 6·2; N, 21·9, 22·0%). On evaporation the chloroform extract (*b*) left 2·5 g. of unchanged bromo-carbamide, and the ethereal extract (*c*) left no residue. The acid ethereal extract (*d*), on drying and removal of solvent, left 8·0 g. of viscous oil, b. p. 140—190°/28 mm., which was not unsaturated and was probably impure *s*-di-α-hydroxybutyrylcarbamide; it was not further examined. On the assumption that 7 g. of the disubstituted carbamide were formed, the total amount of hydrolytic products obtained accounts for almost all the α-bromo-carbamide taken.

Crotonylcarbamide, m. p. 207°, is not very soluble in water, cold alcohol, ether, or chloroform. It resembles its isomeride in not decolorising bromine water in the cold.

The action of 2 mols. of caustic alkali on α-bromobutyrylcarbamide produced an almost quantitative yield of an unsaturated acid mixture which, on treatment with phosphorus trichloride followed by water, was quantitatively converted into solid crotonic acid, m. p. 72°.

Hydrolysis of Crotonamide, m. p. 158°.—A mixture of 8·5 g. of crotonamide with 100 c.c. of *N*-sodium hydroxide was heated on the steam-bath for 30 minutes. On cooling and extracting the product with benzene, no unchanged amide was obtained. The aqueous residue, when acidified (Congo-red), gave an immediate precipitate (8·3 g., isolated by means of ether) of crotonic acid, m. p. 70° (theo. yield of acid, 8·6 g.).

Hydrolysis of Crotonylcarbamide, m. p. 234°.—When the carbamide (12·8 g.) was heated on the steam-bath with 100 c.c. of *N*-sodium hydroxide, ammonia was evolved at once. At the end of 45 minutes the still alkaline solution was saturated with sodium chloride and extracted (*a*) with chloroform (*b*) with hot benzene. The aqueous residue, when acidified with hydrochloric acid, gave immediately a precipitate of solid crotonic acid, which was extracted with ether (*c*). On drying and removal of solvents (*a*) and (*b*) gave no residue; (*c*), on drying and evaporation, left solid crotonic acid, m. p. 70—71° (7·4 g., representing 90% of the carbamide taken). The aqueous residue, on neutralisation, evaporation under reduced pressure, filtration from sodium chloride, and addition of concentrated nitric acid, gave characteristic crystals of urea nitrate.

Hydrolysis of Crotonylcarbamide, m. p. 207°.—The carbamide (12·8 g.), treated exactly as its isomeride, gave the following result:

From (*a*) and (*b*) no residue was obtained; (*c*) gave 7·0 g. of a mixture of crotonic acids which did not solidify when kept at 0° for 1 week. On treating this mixture with phosphorus trichloride followed by water at 25—30°, 6·5 g. of solid crotonic acid, m. p. 70°, were obtained. The aqueous residue contained urea.

Attempts to obtain Labile Crotonamide.—(i) *Action of caustic alkali on α-bromobutyramide in the cold.* 4·8 G. of α-bromobutyramide of m. p. 111° were kept for 2 hours in 20 c.c. of *N*-potassium hydroxide. Ammonia was evolved after 10 minutes. The solid, after crystallisation from alcohol, melted at 111° and was unchanged α-bromobutyramide. The filtrate contained traces of halide and cyanide.

(ii) *Action of caustic alkali on α-bromobutyramide at* 100°. A similar mixture was gently boiled, and the gases evolved were passed through 50% sulphuric acid into a solution of semicarbazide in acetic acid. Crystals of propaldehydesemicarbazone (m. p. 150°) soon began to separate from this solution (Found: N, 36·6. Calc.: N, 36·5%) (compare Mossler, *Monatsh.*, 1908, **29**, 69).

(iii) *Action of water on α-bromobutyramide.* After 11 g. of α-bromobutyramide had been boiled for 1½ hours with 35 c.c. of water, 10 g. of unchanged bromo-amide were recovered. The halide in solution corresponded with 1 g. of hydrolysed bromo-amide, but no unsaturated amide could be obtained.

(iv) *Action of sodium ethoxide on α-bromobutyramide.* α-Bromobutyramide (17 g.) was added to sodium ethoxide (2·3 g. of sodium in 50 c.c. of alcohol) and the mixture was refluxed for 1 hour. On removal of alcohol, addition of water, extraction with chloroform, and removal of this solvent after drying, a gum was left which did not crystallise after being kept at 0° for some weeks. The aqueous residue was acidified; ether extracted nothing from it.

In conclusion, the author would like to express his gratitude to Dr. A. J. Ewins and Mr. G. Newbery of Messrs. May and Baker, Ltd., and to Dr. J. Kenyon for their kind assistance and criticism.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, September 20th*, 1926.]

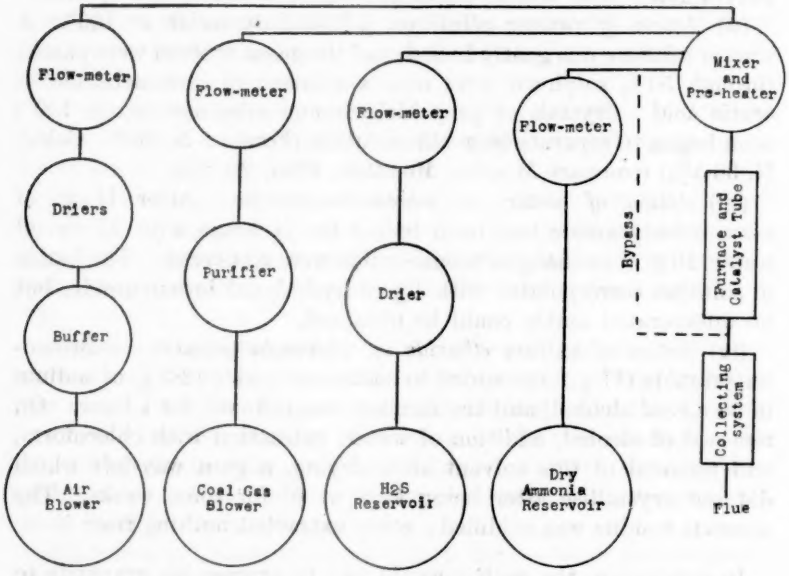
CCCC.—*The Oxidation of Ammonium Sulphide.*

By MALCOLM P. APPLEBEY and JOHN A. LANYON.

THE recovery of ammonia from coal-gas in the form of ammonium sulphate is usually effected by means of sulphuric acid, either by washing the crude gas directly with acid of suitable strength, or by first condensing the ammonia as a dilute liquor from which, after treatment with lime, the ammonia is distilled into the saturator.

It has often been pointed out that the crude gas contains more than sufficient sulphur to furnish the necessary sulphuric acid for the fixation of the ammonia, and several processes have been described by which ammonium sulphate may be obtained without the supply of extraneous sulphuric acid. The process of Cobb, depending on the precipitation of zinc sulphide and its subsequent reoxidation to zinc sulphate, and that of Feld, which is based upon a complex series of reactions involving the conversion of ammonium thiosulphate into tetrathionate and *vice versa*, with the subsequent

FIG. 1.



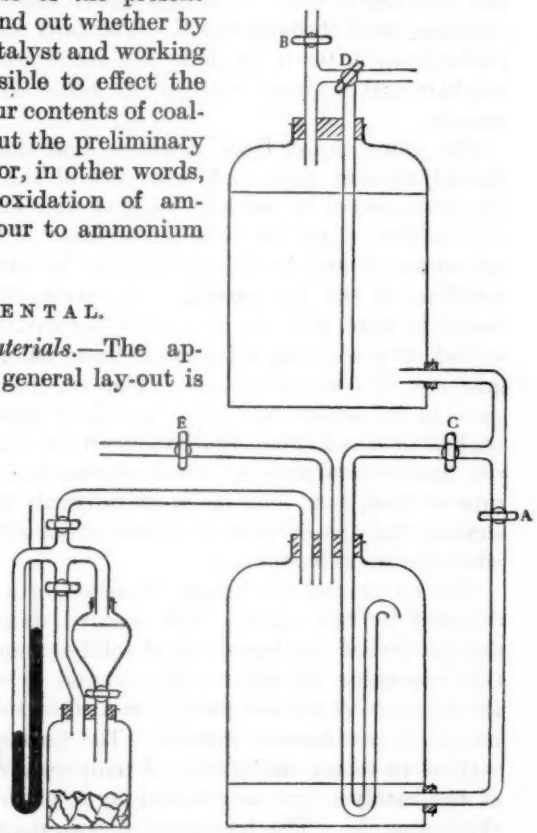
formation of sulphate by decomposition of the tetrathionate (compare Meade, "Modern Gasworks Practice," 1916), have been shown to be commercially practicable. Both, however, are somewhat lacking in simplicity when compared with the usual processes of recovery in which sulphuric acid is used. A process simpler in theory is that of Burkheiser, in which sulphur is first removed by the iron oxide purifier charged with a specially active form of oxide, and then oxidised to sulphur dioxide by a blast of air. Two purifiers are used in an alternate manner, one being occupied in absorbing hydrogen sulphide from the gas while in the other the sulphur is being oxidised. The sulphur dioxide so obtained is finally united with the ammonia which has been separated at an earlier stage of the process, and the resulting ammonium sulphite

is oxidised in the dry state to sulphate by a current of warm air. The process may be represented by the equations :

(1) (First purifying tower), $Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$.
(2) (Second tower), $2Fe_2S_3 + 9O_2 = 2Fe_2O_3 + 6SO_2$.
(3) $2NH_3 + SO_2 + H_2O = (NH_4)_2SO_3$.
(4) $2(NH_4)_2SO_3 + O_2 = 2(NH_4)_2SO_4$.

The primary purpose of the present investigation was to find out whether by a suitable choice of catalyst and working conditions it was possible to effect the oxidation of the sulphur contents of coal-gas in one stage without the preliminary removal of ammonia, or, in other words, to effect the direct oxidation of ammonium sulphide vapour to ammonium sulphite or sulphate.

FIG. 2.



EXPERIMENTAL.

Apparatus and Materials.—The apparatus of which the general lay-out is represented in Fig. 1 consisted of :

(1) Apparatus for the preparation and storage of the gases employed.

(2) Flow-meters to measure the rate of supply of each gas.

(3) A mixer and pre-heater.

(4) The catalyst tube with its heating furnace.

(5) The collecting system for the solid products.

Air and coal-gas were introduced by means of blowers of the usual laboratory type operated by means of a small filter-pump, the inlet tube of the pump being open to the air in the first case and in the second connected to the gas tap. Ammonia obtained from a cylinder was conveniently stored in and delivered from a bottle of ammonium thiocyanate in the manner described by Foote and Brinkley (*J. Amer. Chem. Soc.*, 1921, **43**, 1178). Hydro-

gen sulphide was obtained in a pure condition by the action of water on aluminium sulphide, freshly prepared from its elements. The reaction was violent and the gas had therefore to be delivered from storage vessels. The apparatus used had some novel features represented in Fig. 2. It enabled several litres of gas to be stored over its saturated aqueous solution, the gas being brought in with taps A and B open and C, D, and E closed. By closing A and B and opening C and D the gas could then be delivered under a constant head through tap E. The taps on the generating bottle enabled the latter to be detached, recharged, filled with hydrogen sulphide and replaced without air being admitted to the storage vessels.

The gases, freed from moisture and dust, were delivered by fine-adjustment taps to flow-meters of the usual capillary type. The flow-meters for air and coal-gas were calibrated by measuring the outflow of gas for different readings of the instruments, those for ammonia and hydrogen sulphide by chemical absorption and weighing of the gas passing in a measured interval. It may be useful to note that the absorbent for hydrogen suphide was lime slaked with a strong solution of ferric chloride and made up into granules of convenient size. This absorbent is rapid and complete in its action and gives excellent quantitative results when backed by a soda-lime tube to absorb the water liberated. None of the flow-meters gave a linear relationship between pressure and rate of flow, but tests made at intervals during the experiments showed that the calibration figures remained satisfactorily constant when the gases were clean.

The mixer and pre-heater consisted of a wide glass spiral surrounded by hot water. This secured uniformity of composition and prevented the deposition of solid ammonium sulphides. From this apparatus the gas mixture passed by a short connexion into the catalyst which was packed in a silica tube of 16 mm. diameter heated in a resistance furnace. The furnace was wired in such a way as to secure uniformity of temperature, and the temperature of the catalyst was ascertained by a platinum–platinum-rhodium thermocouple. The temperature was maintained as constant as possible during a run by hand regulation, but it was recognised that in some experiments where a visible glow occurred in some parts of the catalyst the temperature recorded can only have been a mean. The thermocouple was so placed that it gave the temperature of the last parts of the catalyst to be traversed by the gas. The catalysts used filled the silica tube to a length of 25 cm.

Collection of the Products.—Although most of the ammonium

sulphate obtained solidified as a vitreous mass in the silica tube within 10 cm. of the end of the furnace, the sulphite which the gases contained formed a very fine fume which was not absorbed by water in any form of bubbling apparatus or in a pumice tower 80 cm. long. Eventually it was found possible to collect the fume completely by means of an asbestos mat in a Buchner funnel fitted to the escape tube. In all experiments the fume so collected consisted of pure ammonium sulphite, as the following analyses show; no other sulphur product was detected in the fume:

NH_4 = 31·10, 30·95, 30·49%. Mean 30·85%.
SO_3 (by iodine) = 68·37, 69·00, 68·71%. } Mean 68·82%.
(by $BaSO_4$) = 68·73, 69·12, 69·00%. }
Calc. for $(NH_4)_2SO_3$: NH_4, 31·03; SO_3, 68·97%.

The asbestos mat collector was inconvenient, since it produced an appreciable back-pressure. In view of the evidence obtained of the nature of the fume, it was therefore decided to collect only such portion of the products as would separate in a long, wide exit-tube and to assume that the sulphur not accounted for in this product had escaped as ammonium sulphite. The exit gases in each experiment where this assumption was made were proved to be free from hydrogen sulphide.

The product was scraped out of the collecting tube as completely as possible by means of a nickel spatula and transferred, after being thoroughly mixed, to a weighing bottle. The products were nearly always apparently dry, but in a few cases where they appeared to be moist they were dried in a partially evacuated desiccator.

Analysis.—The ions $NH_4^{\cdot}$, S_2O_3'', SO_3'', SO_4'', and $NH_2{\cdot}SO_2'$ all appeared at various times in the products, as also did elementary sulphur. In the few cases where the ion $NH_2{\cdot}SO_2'$ appeared (the product was coloured yellow by ammonium aminosulphonate and its decomposition products) analysis was not carried out, since it was clear that oxidation was incomplete. The ammonium content was determined by distillation into standard acid. The determination of sulphite, sulphate, and thiosulphate in the product presented great difficulties, and success was only achieved by using the following method suggested by Mr. J. J. Manley, whose advice and assistance we gratefully acknowledge. The method depends on the slow oxidation of sulphite in air and the extrapolation from the iodine titre–time curve to the iodine titres before oxidation began (sulphite plus thiosulphate) and after it was complete (thiosulphate alone). A measured volume of water free from carbon

dioxide * is placed in a large conical flask fitted with inlet and outlet tubes and also with a tube by which a pipette can be introduced for the removal of samples. Air, freed from carbon dioxide and saturated with water vapour by passage through a similar flask, is passed through the water for 2 hours to saturate it with oxygen, a small glass capsule containing a weighed quantity of the solid sufficient to give a solution about 0·15*N* in reducing power is dropped in, the stopper replaced, and the current of air restarted. After a definite time from the addition of the solid the air current is stopped, a measured sample removed and at once run into a measured volume of *N*/10-iodine solution, the excess being determined by thiosulphate. For the first half-hour samples are withdrawn every 5 minutes and afterwards every half-hour until a constant titre is reached. A characteristic example is given in the following table:

Time (mins.).	Iodine (c.c.).	Time (mins.).	Iodine (c.c.).	Time (mins.).	Iodine (c.c.).	Time (mins.).	Iodine (c.c.).
5	19·65	30	16·25	150	9·0	270	6·65
10	18·8	60	13·6	180	8·0	300	6·45
15	18·2	90	11·5	210	7·35	330	6·5
20	17·8	120	9·7	240	6·8	360	6·4
25	16·95						

Extrapolated for zero time, 20·3 c.c.; for infinite time, 6·4 c.c.

This analytical method, although laborious, gave very satisfactory results. Total sulphur was determined by oxidation of the whole by bromine-water and subsequent precipitation as barium sulphate. Elementary sulphur when present was obtained by difference from two estimations of total sulphur as barium sulphate, the first performed on the solid product, the second on the solution in water from which the sulphur had been removed by filtration. It is noteworthy that under the analytical conditions elementary sulphur does not react appreciably with iodine or with sulphite. Specific experiments failed to detect any such action.

Catalysts.—The following catalysts were investigated:

(1) *Burnt pyrites.* This was a commercial specimen from Tharsis pyrites and had the composition: Fe_2O_3, 87·34%; Cu, 2·14% (of which 1·11% was soluble in water, presumably as $CuSO_4$); S, 4·15% (2·43% soluble in water).

(2) *Ferric oxide gel.* Prepared by precipitating a solution of

* Precautions against the entry of carbon dioxide in the air-stream or during the removal of samples by the pipette are necessary owing to the reaction between thiosulphate and unpurified air. Mayr has recently stated that the decomposition is not due to carbon dioxide (*Z. anal. Chem.*, 1926, **68**, 274). The deleterious impurity in air is, however, removed by reagents which absorb carbon dioxide.

ferric chloride by sodium hydroxide. Before use it was dark brown and transparent and showed the characteristic conchoidal fracture of a gel.

(3) *Alumina powder.* (4) *Soft alumina.* (5) *Alumina gel.* These were all prepared by precipitating a solution of aluminium sulphate with sodium carbonate. They differed only in hardness; the hard gel had a conchoidal fracture but was not transparent.

(6) *Bauxite.* The specimen used contained some iron.

(7) *Pumice.* The sample used contained little iron. It was ground to convenient size and freed from dust.

(8) *Chromic oxide.* Some of the pumice used for catalyst (7) was boiled for 20 minutes in a saturated solution of ammonium dichromate, dried, and ignited.

(9) *Chromic oxide gel.* Prepared by precipitating a solution of chromic chloride with sodium carbonate. The gel structure was well defined and was not destroyed at 500°.

Tabulation of Results.—Analytical data for the various products are given under three headings which require some explanation. The values under "Found" are the actual percentages of each constituent determined analytically without any adjustment. In most cases these do not add up to 100% because the products are somewhat hygroscopic and absorb water during the operations of detaching from the collecting tube and mixing. Under "Dry" are the percentages calculated on the assumption that the deficiency was due to water. The justice of the assumption was in several experiments verified by analysis before and after drying in a desiccator. From the total weight of product collected and the "Dry" percentages it was possible to calculate what percentage of the sulphur introduced as hydrogen sulphide had been recovered in the solid product. These figures are given under "Recovery" in the last column of the tables. From the figures of the "Dry" analysis and from the calculated quantities of $NH_4^{\cdot}$ and SO_3'' equivalent to the sulphur not recovered, figures are obtained which are reduced to percentages and tabulated as "Corrected" (for the justification of this procedure see "Collection of the Products" above).

Ferric oxide catalysts. Ferric oxide was known to catalyse not only the Claus reaction ($2H_2S + O_2 = 2H_2O + 2S$) and the oxidation of sulphur dioxide to trioxide, but also the oxidation of ammonia (Maxted, *J. Soc. Chem. Ind.*, 1917, **36**, 777). It was, however, thought possible that by suitable choice of temperature, oxidation of the sulphur content of the gas might be brought about without oxidation of ammonia. On passing a mixture supplying 450 c.c. of air, 50 c.c. of hydrogen sulphide, and 50 c.c. of ammonia per minute over the pyrites catalyst, some reaction occurred at as

low a temperature as 150°, but at no temperature up to 400° was any considerable amount of solid deposited. At all temperatures the solid product was sulphur, formed by the Claus reaction, and the water formed was considerably more than corresponded with the sulphur. It was thus evident that ammonia also was being oxidised, the oxidation being apparently to nitrogen and water since no acidic nitrogen could be detected among the products. With ferric oxide in this form, therefore, ammonia was oxidised before a sufficient temperature was reached to carry the oxidation of hydrogen sulphide further than the Claus reaction.

With ferric oxide gel and an increased supply of air at 195° a small solid product collected, containing principally sulphur and ammonium aminosulphonate. A similar product was obtained at 200°, but it also contained sulphite and thiosulphate. At 235° a bright glow was observed in the front portion of the catalyst and the solid product was very small; much of the ammonia was oxidised. At 250°, there was no solid product and little fume; there was a bright glow and the ammonia was almost completely burnt. The products were again nitrogen and water.

From these experiments it appears that ferric oxide in any form is too active a catalyst in ammonia oxidation to permit its use for the desired reaction. In view of these results some experiments were performed with air and ammonia alone, mainly with a view to establish more certainly the products of oxidation. A very unexpected result was obtained, for it was found that pure ammonia was not oxidised at all on the ferric oxide catalyst between 200° and 300°, although in presence of hydrogen sulphide at these temperatures oxidation is extensive and vigorous. On adding a small quantity of hydrogen sulphide to the entering gas, oxidation began with a glow in the catalyst and continued after the supply of hydrogen sulphide was cut off. Hydrogen sulphide accordingly acts as a promoter for the oxidation of ammonia on ferric oxide gel. In none of these experiments was there any further oxidation of the nitrogen.

Alumina catalysts. Alumina in the form of bauxite is known to be an efficient catalyst for the Claus reaction and, so far as we have been able to discover, is not a catalyst for ammonia oxidation. The first catalyst used was alumina powder, to which the gases were supplied at the rate of 800 c.c. of air, 50 c.c. of hydrogen sulphide, and 100 c.c. of ammonia per minute. This catalyst had the desired properties : in a typical experiment at 230°, the product was white and dry, and completely soluble in water. There was no hydrogen sulphide or sulphur in the products. Analysis gave :

	Found.	Dry.	Corrected.	Recovery.
NH_4	25·60	30·58	30·95	23·9% S
SO_4	6·43	7·68	1·60	
SO_3	24·44	29·20	60·66	
S_2O_3	27·24	32·54	6·79	

The product was thus mainly ammonium sulphite, a large part of which was lost in the very copious fume. The somewhat high proportion of thiosulphate shows that at 230° oxidation had not been carried completely to the sulphite stage. The thiosulphate is formed from sulphur resulting from the Claus reaction.

The alumina powder, though efficient as a catalyst, was mechanically unsuitable, since it produced a considerable back-pressure. Further experiments were accordingly performed with the coarser materials, the gas supply being 650 c.c. of air, 50 c.c. of hydrogen sulphide, and 100 c.c. of ammonia per minute in all experiments afterwards undertaken. The experience gained with alumina powder had shown this to be the optimum mixture.

The following table summarises the experimental results with soft alumina and with alumina gel. Percentages of ammonium are omitted for reasons of space, although they were in each case determined. In most of the products of which analyses are given, the ammonia content corresponded within a few units per cent. with the total sulphur acids found, a slight deficiency in some experiments being traced to the presence of a small amount of ammonium metabisulphite in the product. This fact is in itself a proof that ammonia was not oxidised by this catalyst, since the ammonia supplied was only enough for complete reaction with the sulphur acids.

	Found.			Dry.			Corrected.			Recovery
Temp.	SO_4.	SO_3.	S_2O_3.	SO_4.	SO_3.	S_2O_3.	SO_4.	SO_3.	S_2O_3.	(% S).
					Soft alumina catalyst.					
222°	No appreciable product. Much sulphur deposited in catalyst.									
261	Much sulphur with moisture and aminosulphonate.									
338	3·90	66·60	—	—	—	—*	3·36	66·50	—	88·2
454	11·94	59·28	—	—	—	—	10·69	59·71	—	90·5
479	14·20	54·65	1·34	14·26	54·96	1·35	13·12	56·10	1·24	91·9
527	21·72	49·80	0·66	—	—	—	21·72	49·80	0·66	100
533	24·29	47·40	0·66	24·84	47·82	0·69	18·20	52·46	0·50	75·3
					Alumina gel catalyst.					
395	15·50	47·74	9·78	15·66	48·25	9·89	7·72	58·76	4·89	51·6
424	16·79	51·53	1·70	16·85	51·75	1·80	15·65	52·97	1·69	92·9†
506	17·30	54·40	—	—	—	—	17·30	54·40	—	101·0
550	4·65	65·50	—	4·69	65·76	—	3·72	66·48	—	79·8

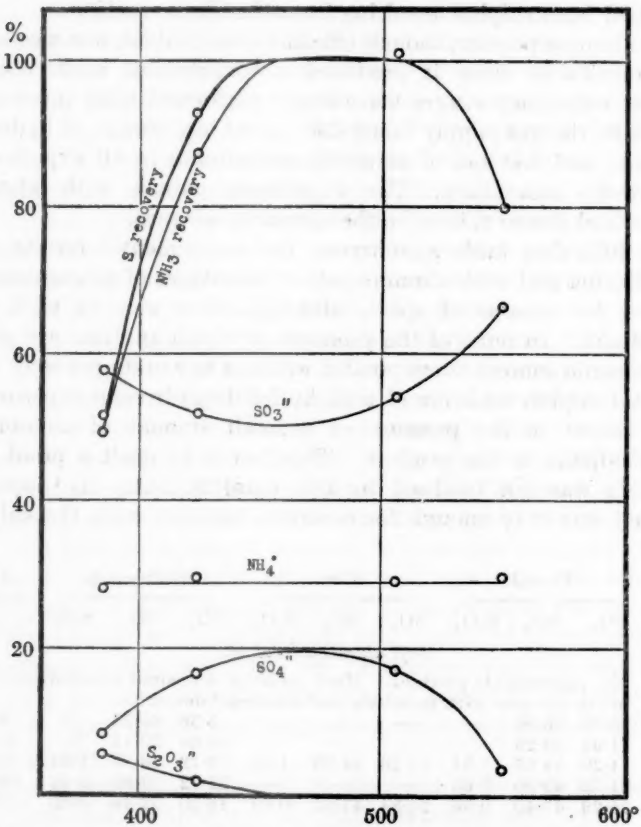
* Where no figures are given under "Dry" the original product contained only a negligible amount of water.

† This product also contained a little free sulphur which was produced during an accidental stoppage of the gas supply.

Fig. 3, which represents the results with alumina gel, shows clearly the effect of temperature on the behaviour of the catalyst. Only one catalyst diagram is reproduced here, but the diagrams of other efficient catalysts are quite similar in general aspect. The noteworthy features are the following :

(1) The percentage of sulphate in the product increases with

Fig. 3.



Alumina gel catalyst ; air 650 c.c. ; H_2S *50 c.c.;* NH_3 *100 c.c. per min.*

temperature to a maximum and then falls off. This is due, first, to the increase in the velocity of the reaction $2SO_2 + O_2 = 2SO_3$ with temperature, and, secondly, to the exothermic character of the reaction.

(2) The efficiency of the recovery increases as the proportion of the less volatile sulphate increases.

(3) The formation of thiosulphate appears to be a low-temperature effect due to the persistence of the Claus reaction.

The activity of ferric oxide in promoting the oxidation of ammonia was again shown in experiments in which we endeavoured to use the mineral bauxite as catalyst. The small percentage of iron contained in the mineral led to almost complete oxidation of the ammonia and no solid products could be collected.

Pumice catalyst. The following results showed that pumice also acted as an efficient catalyst for the oxidation of ammonium sulphide :

	Found.		Dry.		Corrected.		
Temp.	SO_4.	SO_3.	SO_4.	SO_3.	SO_4.	SO_3.	Recovery (% S).
426°	Yield very small.						
470	4·25	65·10	4·30	65·99	3·40	66·60	80·4
553	5·00	65·30	—	—	4·70	65·94	94·8
662	11·75	57·80	12·05	59·21	11·20	59·90	98·0
772	9·70	69·65	9·94	61·20	7·95	62·54	80·2

These results are quite similar to those with pure alumina; the maximum formation of sulphate, however, occurs at a much higher temperature, and the amount is smaller than with alumina, in accordance with the sign of the heat change in its formation.

The data obtained with alumina and with pumice are in accord with the work of Knietsch (*Ber.*, 1901, **34**, 4069) on the kinetics of the contact process, as was shown by a series of experiments in which the ammonia was omitted from the entering gases but added to the products emerging from the catalyst tube. This change of procedure produced no appreciable alteration in the results, proving not only that the ammonia is itself unoxidised by the catalyst, but also that it has no effect on the sulphur dioxide–trioxide equilibrium.

Chromic oxide catalysts. Preliminary experiments with chromic oxide from ammonium dichromate and with chromic oxide gel showed that both materials catalysed the oxidation of sulphur dioxide, the gel being the more effective. On subjecting ammonium sulphide vapour and air to the action of the gel catalyst, however, it was found that chromic oxide, like ferric oxide, was a very active catalyst for ammonia oxidation. Much water was formed, but no solid product. The effluent gases were strongly acid, but the acidity was due to sulphur acids, no nitric acid being detected.

Experiments in Presence of Excess of Coal-gas.—Having established the possibility of quantitatively oxidising ammonium sulphide vapour to sulphite and sulphate, an attempt was next made to apply the process to a mixture approximating in composition to coke-oven gas. For this purpose a gas stream consisting of 650 c.c. of air, 50 c.c. of hydrogen sulphide, 865 c.c. of coal-gas, and 100 c.c.

of ammonia per minute was passed over the alumina gel catalyst. With the dry mixture the following results were obtained :

	Found.		Dry.		Corrected.		
Temp.	SO_4.	SO_3.	SO_4.	SO_3.	SO_4.	SO_3.	Recovery (% S).
510°	16·20	57·50	16·25	57·65	2·20	67·40	13·6
634	15·36	54·70	15·15	54·95	10·41	59·44	66·7

Since the gas from coal distillation is wet, experiments were also performed with the same mixture saturated with water vapour by passing up a 50 cm. tower of wet pumice.

	Found.			Dry.			Corrected.			Recovery
Temp.	SO_4.	SO_3.	S_2O_3.	SO_4.	SO_3.	S_2O_3.	SO_4.	SO_3.	S_2O_3.	(% S).
484°	21·28	37·08	9·06	—	—	—	5·95	59·96	2·55	33·6*
641	16·00	54·10	—	16·23	54·97	—	12·39	58·27	—	76·1

* This product also contained 7·13% of free sulphur, or 2·01% corrected.

In all these experiments the coal-gas interfered seriously with the efficiency of the transformation. The products were smaller in amount and much contaminated with tar, especially at the lower temperatures. At the higher temperatures, a green liquid was found in the collecting system and the products had a strong garlic odour suggesting carbonyl sulphide. On standing, the green liquid deposited a white solid, too small in amount for identification.

It thus appears that, although the oxidation of ammonium sulphide in presence of coal-gas takes mainly the same course as with the pure gas, it does not run smoothly and gives rise to troublesome by-products.

Summary.

1. Ammonium sulphide vapour can be quantitatively transformed to a mixture of ammonium sulphite and sulphate by atmospheric oxidation at temperatures of 450° to 650° in presence of a suitable catalyst.

2. Alumina, best in the form of gel, is the most efficient catalyst for this reaction, but pumice can also be used.

3. Ferric oxide and chromic oxide actively catalyse the oxidation of ammonia, hydrogen sulphide acting as a promoter to ferric oxide.

4. Experimental devices described in this paper include an apparatus for generation, storage and delivery of pure hydrogen sulphide at constant pressure, a quantitative and rapid absorbent for hydrogen sulphide, and a method for the quantitative determination of sulphite and thiosulphate in mixtures of the two.

INORGANIC CHEMISTRY LABORATORY,
OXFORD.

[*Received, September 27th*, 1926.]

The Composition and Characterisation of Genuine Proteins.

HUGO MÜLLER LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY ON OCTOBER 28TH, 1926.

By SØREN PETER LAURITZ SØRENSEN.

MR. PRESIDENT, LADIES, AND GENTLEMEN,

May I be permitted to express to you, Mr. President, and to the Council of the Chemical Society my hearty thanks for the great honour you have shown me in inviting me to deliver the Hugo Müller Lecture this year.

If for the subject of the lecture I am to give to-day I have chosen the problem of the composition and characterisation of genuine protein substances—a problem equally important to Chemistry and to Biology—it is certainly not for the reason that a satisfactory answer can now be given. On the contrary, it will be a long time, and much labour will be required, before this will be possible; but the interest generally taken in the matter, and the discussions concerning the way in which these highly important substances must be assumed to be built up are at present so animated and so many-sided in nature that a brief account of the various points of view from which these questions are dealt with seemed to me to offer some interest to an assembly of English chemists.

The inquiry into the composition of proteins is of a twofold character. In the first place it may be asked which elements enter into their composition, and in what proportions, that is to say, what is the "elementary" composition? When this question has been answered, the next will be the manner in which the different elementary atoms constituting the protein molecule, or the complex of protein molecules, are joined together; in other words, of what compounds of simpler structure are the proteins made up? We shall first contemplate this aspect of the matter.

In the first half of the last century the view advanced by the Dutchman Mulder was generally adopted, according to which all albuminoid matter was composed of one and the same organic substance, which, in consequence of the vital process, underwent various changes, whilst being at the same time combined with different proportions of inorganic substances. Assuming that this nitrogenous substance, this *prima materia* common to all albuminoids, formed the basis of the maintenance of the vital process, Mulder gave it the name of "protein," derived from the Greek verb signifying "to occupy the first place."

As knowledge of the different properties of the different protein substances increased, Mulder's theory of a fundamental substance common to all proteins receded into the background and chemists began to fix their attention upon the decomposition products which can be obtained by the splitting-up of proteins on treatment with acids or alkalis or as a result of enzymatic action.

As far back as 1820 Proust and Braconnot had isolated, from the acid-decomposition products of muscle and glue, leucine and glycine, respectively, to which was added by Liebig, towards the end of the 'forties, a substance obtained from cheese and from horn, namely, tyrosine. It was not until 1865 that the next decomposition product, serine, was isolated by Cramer from silk, and after that time new decomposition products were discovered—often at intervals of many years—so that we now know about twenty different decomposition products of protein substances. Of these products, I shall mention one only, namely, tryptophan, a very important substance isolated by Hopkins and Cole in 1901 from the mixture of products formed by the tryptic digestion of casein.

The decomposition products of proteins are widely different in character, but, with the exception of proline and hydroxyproline, they all have one property in common, in being α-amino-acids, $NH_2 \cdot CHR \cdot CO_2H$.

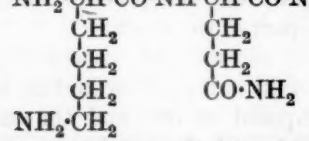
As was shown systematically by Emil Fischer at the commencement of this century, such amino-acids can be united by means of suitable chemical reagents, with separation of water and formation of the so-called peptides:

$$NH_2 \cdot CHR \cdot CO \cdot NH \cdot CHR' \cdot CO_2H$$

Dipeptide.

$$NH_2 \cdot CHR \cdot CO \cdot NH \cdot CHR' \cdot CO \cdot NH \cdot CHR'' \cdot CO_2H$$

Tripeptide.



Residue of lysine. Residue of the amide of glutamic acid.

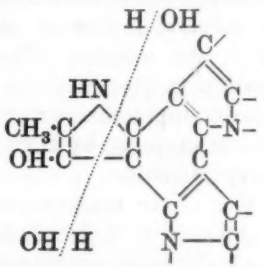
Tripeptide.

Such synthetically-prepared peptides, and more particularly those of complicated structure, resemble in many points the less degraded decomposition products of proteins, the so-called peptones, and consequently it is an obvious conclusion that the proteins consist

essentially of amino-acids, bound together by peptide linkings, –CO·NH–.

This conception of the structure of proteins, which was chiefly based on the very extensive investigations of Emil Fischer, furnishes the most reasonable and plausible explanation of the principal properties of proteins, more especially of the many analogies existing between proteins and amino-acids, and also of the formation of the latter by the decomposition of the former. The view taken by Fischer has indeed, during many years past, formed the general foundation of all researches and reflexions on the composition and structure of protein substances, and only the work done in the most recent years would seem to suggest the necessity of modifying it.

In this connexion, I may first mention the Danish chemist N. Troensegaard, who five or six years ago proposed the view that protein substances are in the main built up of hydroxyl-containing, heterocyclic rings, more especially pyrrole rings. Troensegaard holds that in this way a bridge can be thrown between protein substances on the one hand and the pyrrole-containing compounds —the hæmin of blood and the chlorophyll of plants—on the other. The following formula is given by Troensegaard as representing such a provisional model of a protein ring system :



Troensegaard regards the formation of amino-acids by hydrolysis as taking place in the manner shown by the dotted line in the figure. It will be seen that such a hydrolysis, which requires the entire disruption of the pyrrole ring, will lead to the formation of alanine or, in the case of substitution in the methyl group, of substituted alanines such as phenylalanine, tyrosine, tryptophan, and histidine. By elaborate and ably conducted experiments (chiefly reductive decomposition experiments of different kinds), Troensegaard has of late years endeavoured to prove the correctness of his views; but in my opinion he has not yet succeeded in furnishing conclusive evidence. There can, however, be no doubt—as was also clear to Emil Fischer—that in the protein molecule there exist bindings other than the simple peptide linking, and it is highly probable that a part of the nitrogen which it has not yet been possible to isolate in the

form of known compounds from the hydrolytic decomposition products of a protein substance may exist in such, or similar, easily decomposable, heterocyclic rings as those mentioned by Troensegaard; but it is surely going too far to replace all peptide bindings by heterocyclic rings of this kind.

More compatible with the usual conception, according to which protein substances are complicated polypeptides, is the supposition that diketopiperazine rings may exist in the protein molecule. The simplest of such compounds is, as you know, glycine anhydride (I), and the general formula of the anhydrides of different amino-acids may be written as (II).

(I.) $NH<\begin{matrix}CO-CH_2\\CH_2-CO\end{matrix}>NH$ $NH<\begin{matrix}CO-CHR'\\CHR''-CO\end{matrix}>NH$ (II.)

The possibility of such groups being present in the protein molecule was recognised by Emil Fischer and repeatedly examined by Emil Abderhalden, but its present great interest dates more particularly from the time when, shortly after 1920, R. O. Herzog and his collaborators, basing their views upon Röntgen-spectrographic investigations of high-molecular organic substances, including silk fibroin, tried to prove that the essential substance of silk fibroin is a polypeptide of simple construction or an anhydride of the same, containing only glycine and alanine. They consider that this compound is in all probability glycylalanine anhydride, and consequently is possessed of a diketopiperazine ring. The molecules of the fundamental substance are supposed by Herzog to be combined with one another by secondary valencies.

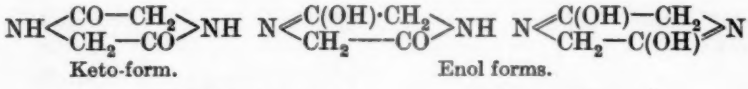
Since then, the question of the existence of diketopiperazine and other similar rings in the protein molecule has been the subject of much discussion and of thorough experimental investigation by Abderhalden, M. Bergmann, and P. Karrer. It would carry us too far to go into all the details regarding this very difficult question, which is as yet far from being cleared up; I should, however, like to mention a few particularly interesting details.

It is Abderhalden who has made the greatest endeavours towards demonstrating the presence of diketopiperazines in proteins. He has succeeded in isolating such substances from the products of protein decomposition and has sought to prove that these anhydrides are not formed from polypeptides by a secondary process. Abderhalden has further studied colour reactions, and oxidation and reduction processes, towards which he finds polypeptides and diketopiperazines behave differently. For example, diketopiperazines, if suitably reduced, yield piperazines—and so also do the protein substances studied by him—whereas the polypeptides do not; and

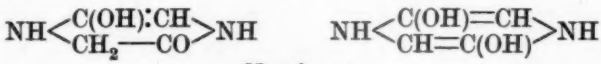
from these facts he draws the conclusion that protein substances must contain the diketopiperazine ring.

Abderhalden's experiments and his interpretation of the results have been the subject of a good deal of criticism, and, as it seems to me, not without reason. In my opinion, the most that can be said is that his researches go to show that at any rate a part of the protein nitrogen is probably present in the form of diketopiperazine rings.

A very important point concerning the structure of protein material is the behaviour of the compounds towards proteolytic enzymes. Waldschmidt-Leitz and Schäffner (*Ber.*, 1925, **58**, 1356) have shown that none of the usual proteolytic enzymes attacks diketopiperazines, whereas polypeptides, as is well known, are readily decomposed by erepsin. This observation implies that no great part of the protein molecule can consist of diketopiperazines, at all events in the usual keto-form. On the whole, the reactivity of the commonly occurring diketopiperazines is too slight and these substances are far from being labile enough to justify the assumption that in the usual keto-form they constitute the main part of such easily changeable substances as the proteins. In fact, Abderhalden has repeatedly pointed out the possibility that the diketopiperazines may exist in proteins not in the usual keto-form, but in some tautomeric, more labile form; indeed, particularly by heating them with aniline, he has succeeded in transforming common diketopiperazines into tautomeric compounds possessing a greater power of reaction and exhibiting properties that suggest the presence of an ethylenic linking. The following are the formulæ given by Abderhalden for these desmotropic—as they are called—2 : 5-dioxopiperazines :



Keto-form. Enol forms.



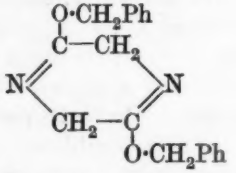
New forms.

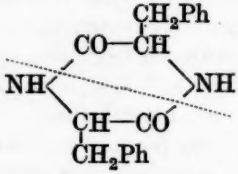
Abderhalden believes that the desmotropic form prepared by him has a double bond between the carbon atoms, but he has no decisive reason for preferring this formula to the usual enol-form. Such proteins as silk fibroin, keratins, and the like, which are very resistant, contain, he supposes (*Z. physiol. Chem.*, 1925, **152**, 89), the stable keto-form, whereas the more labile proteins contain one of the anhydride forms with the double bond. He points out as particularly characteristic that the labile glycine anhydride prepared by him is converted into the keto-form by simple heating in aqueous

solution at 90—100°, and it is undeniable that such a reaction reminds one of the denaturation of proteins by heating.

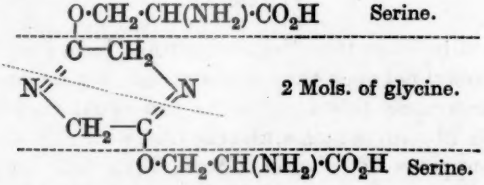
The question of labile nitrogenous rings forming the fundamental structure of proteins has been dealt with also by other investigators from similar standpoints and on the basis of the results obtained in Röntgen-spectrographic researches on substances of high molecular weight. I will mention only a few of the most prominent of these inquirers.

Karrer, Gränacher, and Schlosser (*Helv. Chim. Acta*, 1923, **6**, 1108) have shown that the silver compound of glycine anhydride, if treated with benzyl chloride on a boiling water-bath, yields the *OO'*-dibenzyl ether of dihydroxydihydropyrazine (III), which possesses quite different properties from those of the well-known anhydride of phenylalanine (IV). In contradistinction to phenylalanine anhydride, the new compound can be very easily decomposed

(III.) 

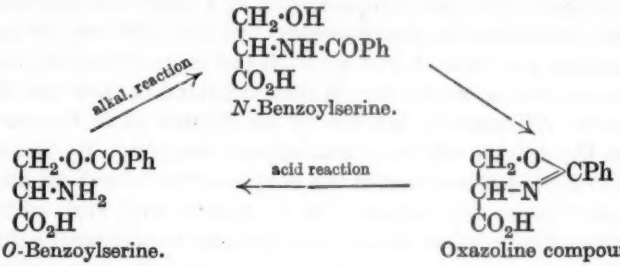
 (IV.)

by being heated in an acid liquid, with formation of glycine and benzyl alcohol. The authors, directing attention to the great lability and power of reaction possessed by such compounds in comparison with common amino-acid anhydrides, say: "Die Vorstellung, dass ein physiologisch so ungemein aktiver und wandelbarer und chemisch labiler Stoff wie das Eiweiss nur aus verhältnismässig reaktionsträgen und beständigen Polypeptidketten und Diketopiperazinringen aufgebaut sei, kann schwerlich befriedigen." More particularly can hydroxyamino-acids be easily formed by hydrolysis of compounds of the type here referred to, as will appear from the formula given below of a substance which will yield serine and glycine by hydrolysis.



In this connexion the wide-ranging experimental researches of M. Bergmann and his collaborators are of paramount interest. As a perspicuous example, I may mention the investigations of Bergmann and Mickeley (*Z. physiol. Chem.*, 1924, **140**, 128) on the

displacements which take place in benzoylserine. They may be expressed in the following form :



If *N*-benzoylserine is treated with diazomethane, the methyl ester will be formed, and this compound, on treatment with thionyl chloride, even in the cold, yields, by loss of water, an oxazoline compound which is stable in alkaline solution and can therefore be saponified with formation of a salt of the oxazoline compound as depicted in the table. As soon as the liquid is rendered acid, however, hydration begins, with formation of *O*-benzoylserine. This compound is stable only in acid solution; as soon as the liquid becomes alkaline, a transformation to the original *N*-benzoylserine takes place. I will not go into the question as to the cause of these transpositions, but will only mention that if the benzoyl group in *N*-benzoylserine is replaced by the radical of glycine, $NH_2 \cdot CH_2 \cdot CO-$, we arrive at the formula of common glycylserine, on which also Bergmann has been working. The state of things here is rather more complicated, yet even in this case it has been proved possible to prepare compounds which by a mere alteration of the reaction of the solution are converted into isomeric substances. Bergmann says indeed: "Ich halte es für sehr wahrscheinlich, dass solche Oxazoline oder analoge instabile Ringsysteme am Aufbau der natürlichen Proteine beteiligt sind" (*Naturwiss.*, 1924, **12**, 1158).

The researches of which I have now given a somewhat condensed and necessarily incomplete account, and all of which date from the last few years, are extremely interesting. It has been emphasised with perfect justice how desirable, indeed how necessary, it is for the comprehension of many of the transformations of protein substances to be able to point out labile bindings—I need here mention only the denaturation process, still obscure, which many soluble proteins undergo on heating or on treatment with alcohol.

But a question now arises which in my opinion it is absolutely necessary to subject to a closer examination before we may draw decisive conclusions as to modern ideas regarding the structure of protein substances; this is the question how compounds having

the assumed structure will behave towards proteolytic enzymes. Concerning this problem, as far as I am aware, this only is known with certainty, that diketopiperazines, as I have mentioned above, in contradistinction to polypeptides, are not split up by erepsin. The question can now be put with all the more stringency because the investigations made by Waldschmidt-Leitz and his fellow-workers in Willstätter's laboratory at Münich have thrown more light on the specific effects of proteolytic enzymes. By means of a suitably effected adsorption of the enzymes (the adsorbent used was aluminium hydroxide prepared in a definite way) and subsequent convenient elution it has been proved possible to prepare the different proteolytic enzymes in a state of more perfect purity than was hitherto known. By this procedure it has now been shown—as stated in the table below—that all the peptides experimented upon

Enzyme-specificity.

— = no action. + = action. ++ = marked action.

	Enzyme.		
	Erepsin.	Trypsin.	Trypsin + enterokinase.
1. Alanylglycine	+	—	—
2. Glycyltyrosine	+	—	—
3. Glycylglycine	+	—	—
4. Glycylalanine	+	—	—
5. Leucylglycine	+	—	—
6. Leucylalanine	+	—	—
7. Leucylglycylglycine	+	—	—
8. Peptone (*ex* albumin, Merck)	—	+	++
9. Clupein	—	+	++
10. Thymus histone	—	+	++
11. Caseinogen	—	—	+
12. Fibrin	—	—	+
13. Gelatin	—	—	+
14. Gliadin	—	—	+
15. Zein	—	—	+

are split up by erepsin, whereas none of them—not even a tripeptide which was formerly considered to be decomposable by trypsin—is split up by the enzyme trypsin. It will further be seen that the field of activity of erepsin is confined to the simple peptides: neither peptone, protamine histone nor any of the comparatively complex proteins can be split up by erepsin. On the other hand, all these substances are split up by trypsin after the latter has been activated by means of enterokinase: in no case, however, can trypsin be replaced by erepsin, or *vice versa*.

This view must, however, undergo some alteration in consequence of the investigations recently published by E. Waldschmidt-Leitz, A. Schäffner, and W. Grassmann (*Z. physiol. Chem.*, 1926, **156**, 68) on the effects successively produced on clupein by different proteolytic enzymes. Indeed, it is shown that if the consecutive

order of the enzymes employed is changed, results are obtained which are inconsistent with the supposition that each enzyme possesses an absolutely specific character. The degree of specificity seems, on the contrary, to be dependent not solely on the different amino-acids which enter into the polypeptide complex concerned, but also on some other factors, as yet unknown.

In one point, however, the two enzymatic scissions resemble each other. In both of them free carboxyl groups are formed (measurable by formol titration or by Willstätter's titration) and amino-groups (measurable by van Slyke's or by Folin's method), and in the case of the simple polypeptides, where such a test is practicable, the formation of carboxyl and amino-groups takes place in equivalent quantities. This may be, and has hitherto been, accounted for by assuming a splitting-up of peptide linkings, and no evidence has yet been furnished to prove that the new cyclic compounds assumed to enter into the composition of proteins admit of being split up by trypsin or erepsin with formation of carboxyl and amino-groups.

In peptic scission, it has long been known that the effect is far less radical. Most of the natural protein substances are attacked, at any rate after denaturation, by pepsin; but the decomposition, measured, say, by means of formol titration, is only slight, whilst on the other hand the properties of the substances are greatly altered. What really takes place here is not yet known with certainty; it would seem, however, that it is something more than a splitting-up of a few peptide linkings. In this respect some experiments published this year by H. Steudel and his collaborators (*Z. physiol. Chem.*, **154**, 21, 198) are of considerable interest. In the peptic scission of a number of proteins these investigators find a far greater increase of carboxyl groups than of amino-groups; but they too are unable to give a definite explanation of this fact. From some very recent experiments of E. Waldschmidt-Leitz and E. Simons (*ibid.*, **1926**, **156**, 114) it appears, however, that in the peptic scission of certain proteins (casein, egg-albumin, and *Ricinus* globulin), in the first stages at least, equivalent quantities of carboxyl and amino-groups are formed.

Regarding the actual state of affairs, it seems to me premature to assume that the protein molecule is composed in the main of heterocyclic rings. Besides the well-known heterocyclic rings (the indole ring in tryptophan, the iminazole ring in histidine, and the proline ring) it is highly probable that there exist smaller proportions of other heterocyclic rings; however, I still consider the peptide linking the principal one.

It is quite another question whether or no the protein molecule may reasonably be supposed to consist of one large polypeptide

complex. According to the Röntgen-spectrographic researches, the fundamental substance in the crystalline part of silk fibroin appears to have a simple structure; but it may just as well be a dipeptide as a diketopiperazine ring. Something similar, though often considerably more complicated, may be the case with other proteins, which accordingly would have to be considered as consisting in the main of larger or smaller polypeptide complexes, bound together by secondary bindings or by mutual salt formation taking place, without any real chemical reaction, between the complexes. Such complexes loosely knit together would act in solution as a co-ordinated whole and consequently exert but a very slight osmotic pressure, as, in fact, is the case. The view here advocated also accounts for the remarkable behaviour with regard to solubility and fractional precipitation of the albumins and globulins in salt solutions.

In an earlier paper (*Compt. rend. Trav. Lab. Carlsberg*, 1923, **15**, No. 11; *J. Amer. Chem. Soc.*, 1925, **47**, 457) I accounted for the solubility of serum globulins and tried to show that these remarkable phenomena can be explained, not on the assumption that we have to do with mixtures of different globulins, but only by assuming these different globulin complexes to be loosely combined with one another in a larger whole, to which I assigned the formula E_pP_q. This was intended briefly to express that the different globulins contain different numbers of euglobulin complexes (E) and pseudoglobulin complexes (P), thus accounting for all that seemed strange in the solubility and precipitation relations.

Later on, in explaining the results of a series of fractionating experiments on casein, Linderstrøm-Lang at the Carlsberg laboratory has successfully used the same view.

If, however, we are to get to the bottom of the matter in the examination of these complexes, without splitting them up, the first thing to be done is an intensive fractionation, and it is of supreme importance that the protein to be used for this purpose shall be really pure or at least as pure as it can be obtained without loss of its characteristic properties.

We here encounter the second question upon which I should like to touch to-day, namely, the characterisation of the individual protein substances. As this question is bound up with that of the elementary composition of proteins, I beg leave to say a few words about it.

As is generally known, all proteins contain the elements carbon, hydrogen, oxygen, and nitrogen; and most of them also small quantities of sulphur and phosphorus. The different proteins have approximately the same percentage composition, it is true; but

nevertheless the differences, and more particularly those in the nitrogen, sulphur, and phosphorus contents, are so considerable that when we come to characterise the individual groups the percentage composition is of valuable assistance. The content of sulphur is but slight, and that of phosphorus generally quite minimal, and the question therefore arises whether we have here to do with integral constituents of the protein molecule itself or of the molecular complex, or whether the sulphur- or phosphorus-containing compounds are only loosely bound, say by adsorption, to the real protein, with the characteristic properties of which these foreign substances have nothing to do. It is quite natural to make such reflexions, particularly if dissolved proteins are considered as composed of a number of complexes loosely knit together, the mutual binding relations of which are liable to be altered by alterations in the temperature, hydrogen-ion concentration, salt concentration, etc., of the solution. It would take too long to go into this question in great detail; I shall have to confine myself to trying to throw some light upon the subject by the aid of a few examples relating to the phosphorus content of proteins.

Setting aside nucleoproteins and their degradation products, the nucleic acids, which, as you know, occupy a peculiar position in the chemistry of proteins, the phosphorus content of proteins shows variations from infinitesimal amounts up to 1% of the dry substance. Those among these proteins which contain the highest amount of phosphorus, and which in several points exhibit similar or identical properties, have been united under the common designation of phosphoproteins or phosphoproteids, the principal representative of which is casein. In regard to the other proteins, it is, rather implicitly, believed that the phosphorus content originates in impurities, probably adhering phosphatides (lecithin and the like). I doubt, however, whether this question can be settled in so simple a manner, and I should like to make good my doubt.

Common casein, prepared and carefully purified by Hammarsten's method, contains about 0·8% of phosphorus and about 15·6% of nitrogen, *i.e.*, about 50 milligrams of phosphorus per gram of nitrogen. The inquiry now arises whether the whole of this phosphorus belongs to the casein molecule as an integral constituent, or whether, by further purification or by an appropriate fractionation of the casein, the phosphorus content can be diminished without the casein losing its characteristic properties. This brings us to the question what is the best definition of casein, or, in other words, how this substance is to be most correctly and most exhaustively characterised. For this purpose we may choose the old familiar reaction—the conversion of casein into the insoluble calcium salt of

paracasein by addition of a soluble calcium salt and a rennet solution (an extract of the mucous membrane of calf's stomach)—which is specific and particularly suitable for the characterisation of casein.

As I have already mentioned, Linderstrøm-Lang has succeeded, by suitable fractionation, in separating casein into several fractions having differing properties, *e.g.*, different solubilities in hydrochloric acid containing sodium chloride, the phosphorus contents being likewise different, and varying from a little more than 50 mg. down to less than 20 mg. of phosphorus per gram of nitrogen. Yet all the fractions gave the characteristic rennet reaction. Which phosphorus content is, then, to be considered as the normal one of casein? Or still more precisely: Is it possible to prepare a casein free from phosphorus and nevertheless able to give the rennet reaction?

If as examples of proteins poor in phosphorus we take globulin and albumin derived from white of egg and horse's serum, it will be found that these substances present a most peculiar picture, which I have broadly outlined in the table below. All the substances had

Phosphorus content of albumins and globulins.

	Mg. P per g. of total N.		Solubility in Am_2SO_4 solution under certain conditions.
	P coag.	P precipitable by alcohol.	Increasing content of P.
Egg-globulin	2	—	—
Egg-albumin	7·5	Whole amount of coag. P.	Constant.
Ordinary serum-euglobulin	2—40	$\frac{1}{10}$—$\frac{1}{50}$ amount of coag. P.	Decreasing.
Ordinary serum-albumin ...	0·3—1·5	$\frac{1}{10}$—$\frac{1}{50}$ amount of coag. P.	Increasing.
Serum-albumin after treatment with alcohol–ether at −4°.	0·04	Almost the whole amount of coag. P.	

been carefully purified by a long succession of precipitations and dialyses, or in the case of albumins by repeated crystallisation. As to the egg-proteins, you will notice that the albumin has a higher phosphorus content than globulin; with respect to serum proteins, the case is quite the reverse. In the egg-albumin, prepared and recrystallised in the usual manner, the phosphorus content is practically constant and appears to be intimately bound up with the rest of the molecular complex of the egg-albumin, as the whole amount of phosphorus is precipitated along with the latter, whether the precipitation be effected by heating or by means of alcohol. The case is quite different with the serum proteins, where only a small part of the whole amount of coagulable phosphorus is precipitable by alcohol. Hence it is probable that—in harmony with

what was formerly assumed—the substances concerned are but loosely associated with the serum-protein complexes. The question whether these substances are to be looked upon as impurities or as belonging to the albumin or globulin complex must, in my opinion, be settled by an inquiry into the possibility of removing them without depriving the albumin and euglobulin of their characteristic properties. In this connexion, I regard it as particularly important that the albumin should be capable of crystallising (a property which it is apt to lose at the slightest alteration) and that the euglobulin should preserve its well-known property of being only slightly soluble or quite insoluble in water, but soluble in weak salt solutions, from which it can again be precipitated by addition of water.

Fortunately we possess a trustworthy method by which practically the whole amount of coagulable phosphorus can be removed from serum without detriment to the above-mentioned characteristic properties of the albumin and the globulin. The procedure was first indicated by W. B. Hardy and Mrs. S. Gardiner (*J. Physiol.*, 1910, **40**, 68) and later employed by E. G. Young (*Proc. Roy. Soc.*, 1922, *B*, **93**, 15), and consists in precipitating the serum at —4° by alcohol, after which the precipitate is thoroughly treated at the same temperature with alcohol and ether. With respect to the serum proteins, the materials in question must therefore be nothing more than impurities, and not integral constituents at all, so that the phosphorus content can scarcely be held responsible for the rather strange fact that under certain conditions euglobulin becomes less soluble in an ammonium sulphate solution the greater its phosphorus content is, whilst the serum-albumin behaves conversely.

I have tried to purify egg-albumin too by treatment with alcohol and ether at —4° and even lower temperatures, but could not extract any phosphorus; the egg-albumin was completely denatured, and the denaturated substance contained, just as it did before the treatment, 7·5 mg. of phosphorus per g. of nitrogen. I may add that by such a treatment casein also fails to give up phosphorus-containing substances to the alcohol.

In this respect, therefore, there seems to be an essential difference between the two albumins, serum-albumin having to be regarded as free from phosphorus, whilst egg-albumin is to be looked upon, for the present at least, as a phosphorus-containing substance.

In some memoirs on egg-albumin published by me some ten years ago, I tried, upon the basis of my measurements of the osmotic pressure of egg-albumin solutions, to determine the weight of the molecule or molecular complex of egg-albumin in the anhydrous state, and at a rough estimate the molecular weight was found to be approximately 34,000, corresponding to a content of about 380

nitrogen atoms. This molecular weight agrees well with that (33,200) found last year by E. J. Cohn (*Physiol. Reviews*, 1925, **5**, No. 3, p. 359), who supposed two tryptophan groups to be present in the molecule, and also tallies with that recently obtained by I. B. Nichols, who found the molecular weight of well-purified egg-albumin to be between 33,000 and 35,000 by Svedberg's centrifugal method (*Z. physikal. Chem.*, 1926, **121**, 76).

If, then, the molecular weight is taken to be 34,000 and the number of nitrogen atoms to be 380, a simple calculation based on the assumption that there is one atom of phosphorus in the molecule would demand a content of 5·8 milligrams of phosphorus per gram of nitrogen. As you will see, the order of magnitude of the phosphorus content found (7·5) agrees fairly well with this estimate; the discrepancy, however, much exceeds the possible error of analysis. I have therefore tried in different ways to reduce the phosphorus content of egg-albumin without depriving it of its characteristic capacity of crystallising. As I have already mentioned, the reduction is not practicable by treatment with alcohol and ether at low temperatures. Neither have I succeeded by fractional crystallisation at different hydrogen-ion concentrations; the phosphorus contents of the different fractions varied only from 7·52 to 7·78 milligrams per gram of nitrogen.

Phosphorus content of egg-albumin.

	Mg. of P per g. of N.
Ordinary egg-albumin	7·5
Fractionated „	7·52—7·78
Electrodialysis:	
Anode liquid	*ca.* 8·5
Inner liquid	7·0—5·0
Stored in ice	7·3—4·7
Calculated for 1 atom of P per 380 atoms of N	5·8

Better results were achieved by electrodialysis, in Pauli's apparatus, of egg-albumin solutions poor in electrolytes. I used two collodion membranes and placed the albumin solution between them. The membranes were impermeable to egg-albumin when no current was passing through the liquid; but as soon as the circuit was closed, egg-albumin began to penetrate through the membrane near the anode, whereas the cathode liquid remained free from albumin for several days. I shall not have sufficient time to go into this remarkable phenomenon at greater length, but will only mention that I always found, relative to the nitrogen content, a larger quantity of phosphorus in the anode liquid than in the remaining inner liquid. When care was taken that the egg-albumin solutions contained but minimal amounts of electrolytes during the electrolysis, the albumin

both in the anode liquid and in the inner liquid could be made to crystallise, and even after repeated crystallisations the phosphorus content of the albumin in the anode liquid was found to be a little higher than usual (about 8·5 mg. P per g. N), whereas the albumin from the inner liquid showed a lower phosphorus content (varying from about 7·0 to 5·0 mg. P per g. N).

Finally, I may mention that, when egg-albumin solutions—especially if dialysed and consequently poor in electrolytes—are stored in ice and saturated with toluene (in order to prevent putrefaction), a part of the albumin will separate in a denaturated state after some time. After the precipitate is filtered off, the albumin remaining in the solution shows normal properties and a normal osmotic pressure: it crystallises readily in the normal manner. The egg-albumin thus obtained and repeatedly crystallised, contains, however, less phosphorus than that newly prepared, and the less the longer it is kept. The phosphorus contents of the samples examined by me varied from 7·3 to 4·7 milligrams per gram of nitrogen; the latter figure refers to a dialysed egg-albumin which had been stored in ice for eleven or twelve years and yet crystallised very nicely and readily after filtration. Thus, as you see, it is possible to prepare well-crystallised egg-albumin with a lower phosphorus content than the normal. The phosphorus content, however, is always very different in order of magnitude from that of serum-albumin, and, as I have already said, I am still of opinion that the large molecule of egg-albumin contains one phosphorus group.

In conclusion, for the sake of preventing any misunderstanding, I may add that I do not regard the crystallisability of albumins and the capacity of casein of forming a coagulum with rennet as affording a complete characterisation of the proteins concerned. As I have lately remarked in a brief note * dealing with this problem, I look upon these properties as *necessary* but not, when taken alone, as "*sufficient*" criteria.

I have been able to give here but a brief account of some of the diverse problems which, at the present moment, occupy the attention of those engaged in a study of the chemistry of proteins, but I trust that it has conveyed an adequate impression of the perseverance with which the intense endeavours are being made in many branches of Science to add to our knowledge of these extremely important substances.

* S. P. L. Sørensen: "Proteins, Lectures given in the United States of America in 1924" (The Fleischmann Laboratories).

CCCCI.—*The Ignition of Gases by an Explosion-Wave. Part I. Carbon Monoxide and Hydrogen Mixtures.*

By Colin Campbell and Donald Whitley Woodhead.

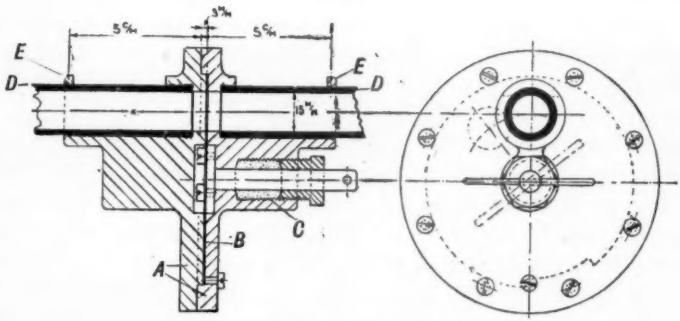
Dixon and Walls (J., 1923, **123**, 1025), in measuring the velocity of detonation of carbon monoxide–oxygen mixtures, observed that the velocity, measured between two time-bridges in a long coiled tube, depended on the distance which the flame had travelled in the same mixture before it reached the first bridge. When the mixture $2CO + O_2$, saturated with water vapour at room temperature, was ignited by the explosion-wave set up in electrolytic gas, the first bridge being 10 cm. from the point at which the two mixtures were in contact, the velocity recorded was 1673 m./sec.; when a loop of tubing, 2·4 metres long,* filled with the carbon monoxide mixture, was inserted before the first bridge, the observed rate was 1708 m./sec. It was believed that the carbon monoxide mixture was not immediately detonated by the wave in the electrolytic gas and that the retarded flame, moving slowly for a short time, eventually recuperated and reached its full rate after travelling about 2·4 metres. The experiments were made with lead tubes (12·5 mm. in diameter), and no direct observations of the slow flame were possible. The experiments now described were made in glass tubes and photographic methods were adopted.

The apparatus consisted of a series of metal and glass tubes of uniform internal diameter (15 mm.) forming a continuous horizontal gallery through which flame passed in front of a drum-camera; one portion of the gallery contained the igniting mixture (usually electrolytic gas) and the other the carbon monoxide mixture to be ignited. Separation of the two mixtures up to the moment of firing was effected by a metal shutter. The igniting mixture was fired by a jump-spark, and the flame traversed first a lead tube 2·8 metres long and then a thick-walled glass tube 50 cm. long, these being cemented together; having now reached its full detonating rate, the flame passed through the shutter apparatus into another glass tube containing the second mixture. To the end of the last tube (the " experimental tube ") was fitted a filling-stopper which could be quickly detached. All the joints were made with cement and were rigid and internally smooth; irregularities which might give rise to accelerations or retardations of flame speed were avoided (see Campbell, J., 1922, **121**, 2483).

* The length given in the original paper was 1·4 metres; Prof. Dixon informs us that this was a clerical error.

The shutter apparatus (Fig. 1) consisted of two outer brass casings, *AA*, bolted together round a flanged edge and surrounding a circular brass plate, *B*, 1 mm. thick, which contained a circular aperture 15 mm. in diameter. The plate could be rotated to a limited extent about a horizontal axis by means of a handle which passed through a stuffing-box, *C*. In the *off* position, the plate formed a complete barrier between two glass tubes, *DD*, which were cemented into supporting sleeves, *EE*; in the *on* position, the aperture coincided with similar apertures in the outer casings. The plate was as thin as possible consistent with the strength required to allow the evacuation of one side of the gallery. Two vulcanite rings were recessed into the interior faces of the outer casings, concentrically with the apertures, and we were then able

FIG. 1.



Mechanical arrangement of the shutter.

to reduce the pressure on one side to 1 mm. Hg whilst the other side was at atmospheric pressure.

In carrying out an experiment the gallery was evacuated and then the respective mixtures were allowed to enter the two sections of the apparatus at equal rates until each was at atmospheric pressure; this process of evacuation and filling was twice rapidly repeated. In order to avoid any mass movement of gas on the opening of the shutter, the two portions of the gallery were put into communication for a moment with the outside air through long leading-tubes. The tap beyond the spark-gap was closed, the further end of the experimental tube opened, the shutter rotated to the *on* position, and the gases were fired; the time taken in the last three operations did not exceed 2 seconds and therefore diffusion at the point of contact of the two mixtures was very slight.

The photographs were taken on films attached to a drum, of 1 metre circumference and 45 mm. edge, which was rotated at

about 40 revolutions per second. The speed of the wheel was calculated with an accuracy of 1—2% by timing the making of an electrical circuit in a mechanism attached to the drum spindle; the calculations of the flame speeds from measurements of the photographs were of the same order of accuracy.

The wall of the experimental tube was about 3 mm. thick, and the length of the longest obtainable was 140 cm.; such a tube was not usually shattered when a detonation-wave passed through it, but was invariably broken when a detonation-wave was actually initiated in it. In some experiments a very long experimental tube was required; this was formed by placing two tubes end to end and cementing them together in a glass or metal sleeve; the junction was made as smooth as possible internally and the velocities of flames passing through it did not appear to suffer any change. Since slow flames are readily affected by slight obstructions in their path (*vide infra*), single tubes were used whenever possible. In order to follow the progress of the flame in a long tube, different portions of the gallery were photographed in successive experiments made under similar conditions.

The carbon monoxide was prepared by the action of hot concentrated sulphuric acid on formic acid; after being washed with caustic potash, the gas had a purity of 98·5%, the remainder being nitrogen. No hydrogen was ever found. Oxygen was either obtained from a cylinder, in which case it contained a small amount of nitrogen, or prepared by heating potassium permanganate; no differences in the results of the experiments were detected. The mixtures were analysed in a modified form of the Bone–Wheeler apparatus and were stored over water at temperatures ranging from 15° to 18°; the amount of water vapour was therefore between 1·6 and 2·0%.

Initial Experiments.

It was shown by two experiments with electrolytic gas that the construction of the shutter and the method of filling the gallery had no effect on the velocity of a flame passing through the apparatus; in the first, the shutter was kept open and the whole of the gallery swept out by the mixture, whilst in the second each side was evacuated and filled separately with the same gas. There was no change in flame velocity in either experiment. When the igniting side of the gallery was filled with electrolytic gas and the other side with the mixture $2H_2 + 3O_2$, the velocity of the flame fell uniformly from that of the igniting gas (rate of explosion-wave, 2820 m./sec.) to that of the ignited mixture (2090 m./sec.) over the first 10 cm. from the junction. Similar results were obtained when the mixture $2H_2 + 5O_2$ (1810 m./sec.) was fired by electro-

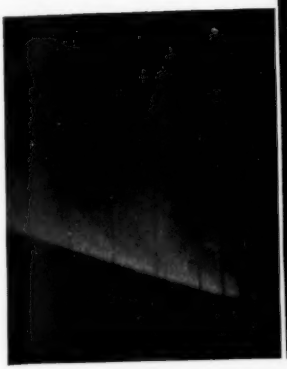


FIG. 2.

FIG. 3.

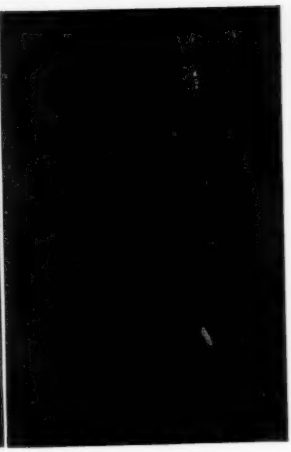


FIG. 4.

FIG. 6.

FIG. 7.

FIG. 8.

FIG. 9.

FIG. 10.

FIG. 11.

[*To face p.* 3012.]

lytic gas, and when $2H_2 + 3O_2$ was fired by $6H_2 + O_2$ (3530 m./sec.). Fig. 2, which is a photograph of the last experiment, shows the gradual change in velocity as the flame passed through the shutter from one mixture to the other. (The broad vertical band in the photograph denotes the position of the shutter.) When the second portion of the gallery contained air or nitrogen (Fig. 3) the electrolytic flame was projected into the inert gas and still affected the photographic film when it had travelled 40 cm. past the shutter; the flame front was not well defined and showed a rapid fall in velocity. This photograph shows the forward movement of the burning gas, then a period of rest followed by a swinging back (compare Dixon, *Phil. Trans.*, 1903, **200**, 315). In one experiment, when a small amount of air was allowed to remain at the shutter between the two explosive mixtures, the flame appeared to hesitate for a brief period and then to proceed at its full rate in the second mixture. Whether a flame could be projected through a considerable length of air or inert gas and ignite a mixture beyond it is a matter under investigation (compare Lean and Dixon, *Manc. Lit. Phil. Soc.*, 1891, **5**, 16).

The Ignition of $2CO + O_2$ *by Electrolytic Gas (moist gases).*

The flame travelled in the electrolytic gas at the rate of 2820 m./sec., but soon after it entered the carbon monoxide mixture its velocity fell rapidly until, at the point 30 cm. (*i.e.*, 30 cm. past the shutter), it was of the order of 800 m./sec. Acceleration then took place until a velocity of about 1250 m./sec. was reached at 140 cm. Fig. 4 is a typical photograph and shows the flame (moving from right to left) from 10 cm. before to 60 cm. after the shutter. When the longer experimental tube was used, a second smaller retardation was found to occur near 150 cm., and this was followed by acceleration and the setting up of the explosive-wave. In three experiments, detonation occurred at very nearly the same point, *viz.*, 260, 260, and 270 cm., respectively. The details of a number of experiments are recorded in Table I, the mean rates over each length of 10 cm. of experimental tube being given. Curve I, Fig. 5, represents the average velocities of flame (calculated from the rates in Table I) throughout an experimental tube 3·2 metres long; it was obtained by plotting flame speed against distance along the tube. The flame speed falls rapidly from that in the electrolytic gas (2820 m./sec.) to a minimum value of 760 m./sec. over the first 50 cm. of carbon monoxide mixture; an ensuing acceleration is checked at 130 cm. when the flame has attained a speed of 1250 m./sec.; the velocity falls to 1050 m./sec. at 165 cm., and from that point to 280 cm. it cannot be represented by a con-

TABLE I.

Flame speeds (metres per second) in wet $2CO + O_2$.

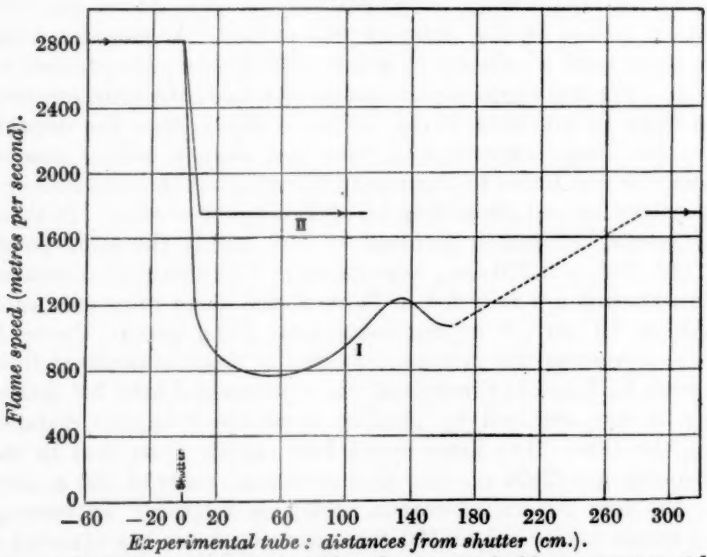
Expt. No.	Distance from shutter (cm.). 5.	15.	25.	35.	45.	55.	65.	75.	85.	95.
234	1560	1000	840	810	780	760			e	
235	1680	1030	870	860	760	760			e	
256			860	770	810	810	810		810	e
257			860	850	790	790	790	790	790	e
193		890	800	800	800	800	800	e		
194				780	780	780	780	e		
195				840	840	840	840	e		
199		920	840	780	760	780	780	e		

Expt. No.	Distance from shutter (cm.). 85.	95.	105.	115.	125.	135.	145.	155.	165.	175.	185.
278	940	940	1100	1200	1270	1270	1100	1030		e	
279	830	880	960	1060	1280	1330	1290	1140		e	
280		900	930	1000	1200	1200	1200	1110	e at 259		
281				1110	1100	1100	1100	1060	1060	1100	1170e
282					1180	1270	1180	1080	1080	1080	1140e

Expt. No.	Distance from shutter (cm.). 215.	225.	235.	245.	255.	265.	275.	285.	295.
298		1360	S		D		e		
299	1080	1270	1400		e				
300		1360	1360	S		D	e		
314			1370	S			D	2000	e

e, end of tube. S, serrated edge. D, detonation.

FIG. 5.



Curve I: *The velocity of flame in* $2CO + O_2$ *(saturated with water vapour at* 15°*) when ignited by detonated electrolytic gas.*

Curve II: *The velocity of flame when* 1% *of the* CO_2 *had been replaced by* H_2.

tinuous curve because of a peculiar variability. This period immediately preceding detonation is of interest in that one or more separate regions of inflammation appear in the unburnt gases in front of the retarded flame proper; the serrated appearance of the flame edge in Fig. 6 was caused by such discontinuous inflammation, three secondary flames appearing within 15 cm. of the point where the explosion-wave was set up. The point of initiation of the wave is indicated by the usual characteristics, *viz.*, an abrupt increase in illumination intensity and the production of a retonation-wave.

If we calculate from the rates given by Dixon and Walls the average velocity of their retarded flame from the point of ignition by the electrolytic gas to a point 2·4 metres along the tube, where detonation was presumed to occur, a value of 1070 m./sec. is obtained. The curve in Fig. 5 gives a value not very different from this, although in the present experiments, which, it should be noted, have been made with straight tubes, detonation did not occur until the flame had travelled about 2·7 metres.

The retarded flame was accelerated more quickly when a small obstruction was placed in the gallery: Fig. 7 was obtained when 1 g. of sand was deposited evenly along 10 cm. of the tube at 130—140 cm. from the shutter, *i.e.*, at the middle of the photograph; the velocity of the flame at 150 cm. was 1500 m./sec., whereas in a similar experiment without sand the rate at the same point was 1130 m./sec. This observation agrees with that of Laffitte (*Compt. rend.*, 1923, **176**, 1392) who found that the distance traversed by the flame in a mixture of oxygen and carbon disulphide vapour before the setting up of the explosion-wave depended upon the condition of the interior of the tube, the distance being shorter when the interior was not perfectly smooth. In Fig. 7, although there was no sharp increase in velocity when the flame reached the sanded portion of the experimental tube, yet there appeared to be a definite and abrupt increase in the rate of reaction as indicated by the relative intensities of illumination. Fig. 8 shows the result of placing in the tube at the points 145 and 165 cm. two hollow cork cylinders (10 mm. internal diameter); the rate immediately before the first obstruction was 1160 m./sec. but increased to 1850 m./sec. within the next 10 cm. It will be observed that the rapid flame had a separate point of initiation at the obstruction previous to the arrival of the slow flame, and it is assumed that the gas was ignited adiabatically by a pressure-wave which had preceded the retarded flame (compare Dixon and Bradshaw, *Proc. Roy. Soc.*, 1907, **79**, 238). The rapid flame did not suffer any marked change in velocity on encountering the second obstruction;

the cork cylinders were ejected from the experimental tube at about 380 m./sec., this value being calculated from the inclination of the dark line in the photograph.

Experiments with Drier Gases.

Dixon and Walls (*loc. cit.*) accepted the efficiency of their drying train when they failed to obtain complete detonation of the dried carbon monoxide mixture after ignition with electrolytic gas, but they did not determine how far, if at all, flame travelled. We have attempted to follow the progress of the flame in carbon monoxide mixtures from which most of the water vapour had been removed. Even if the mixed gases had been completely dried it would have been very difficult to ensure the dryness of the large internal area of the gallery and filling apparatus; no attempt was made, therefore, to secure the degree of dryness attained on long exposure to phosphorus pentoxide. The gallery was dried by passing a stream of warm dry air through it for several hours and then exhausting it for some time by means of a "Hyvac" rotary oil-pump; in this way we were able to reduce the air pressure to less than 1 mm. Hg.

The gaseous mixtures were dried by one of two methods: Method A was to pass the mixture slowly in succession through sulphuric acid, caustic potash, calcium chloride, and a glass worm cooled to $-80°$ into a reservoir containing dry mercury; in a sample of this gas the vapour pressure of the water was less than 0·4 mm. In method B, the gas was passed slowly in very small bubbles through sulphuric acid, through caustic potash and calcium chloride direct to the explosion gallery, the filling operation taking 8 minutes. The flame speeds obtained in these experiments are given in Table II.

TABLE II.

Flame speeds (metres per second) in dried $2CO + O_2$.

Expt. No.	Drying method.	Distance from shutter (cm.). 175.	185.	195.	205.	215.	225.	235.	245.
315	B	1040	980	910	880	850	S		
316	B	1090	1030	950	910	860	860	950	1060
317	B	1020	990	900	880	860	900	930	1090
318	B	1000	910	880	860	880	970	1060	1180

Tube 275 cm. long in each experiment.

Expt. No.	Drying method.	Distance from shutter (cm.). 235.	245.	255.	265.	275.	285.	295.	305.
302	A	S	1640		D e				
303	A			S	e				
304	A			2040	2040	e			
305	A			1990	1990	e			
319	B	860	940	1140	1400	1600	1700	1750	1750e

When method A was used and the experimental tube consisted of two jointed sections, the mixture had detonated before the point 240 cm. (Expts. 304 and 305) or was giving the serrated edge, which, in the "wet" experiments, preceded detonation (Expts. 302 and 303). The measured velocity of detonation in Expts. 304 and 305 is higher than that given by Dixon and Walls for this mixture; in both experiments, the luminous particles behind the wave front appear to be moving towards the open end considerably faster than is usual, and it would seem that the temporary abnormally high rate was due to the increased translational motion of the medium in which the wave was travelling.

When method B was employed for drying, lower velocities were recorded and in no case had detonation occurred at 240 cm. In Expt. 319 the flame had travelled 305 cm. after its initiation and had attained a velocity of about 1750 m./sec., apparently without having reached its full rate. Sometimes the serrated flame edge was more distinct than usual; in Fig. 9 a secondary flame originated at a point 15 cm. in advance of the retarded flame and moved as a whole towards the end of the tube. This movement confirms the previous suggestion that the gaseous medium had a marked translational velocity in front of the advancing flame. Moreover, the motion may be greater than is immediately apparent, since the inner face of this single secondary flame is itself serrated, a number of distinct tongues of flame being formed before there is coalescence with the primary inflammation. At the point of coalescence a rapid rise in the rate of reaction is indicated by increased luminosity and this brighter zone travelled backwards into the burning gases in the form of a wave and, apparently, in much the same way as a wave of retonation.

It is of interest to compare the above results of experiments on the ignition of well-dried carbon monoxide–oxygen mixtures with those of previous workers. Dixon (*Phil. Trans.*, 1893, **184**, 97) gave 1264 m./sec. as the rate of explosion of the well-dried mixture $2CO + O_2$; Girvan (*Proc. Chem. Soc.*, 1903, 236) has shown that, when the theoretical carbon monoxide–oxygen mixture had been cooled to $-50°$, the pressure of aqueous vapour being 0·05 mm., powerful sparks could initiate an "explosion" which travelled slowly down a tube. Wartenburg and Sieg (*Ber.*, 1920, **53**, 2192) found that, although a partial water pressure of at least 0·5 mm. was needed to promote an explosion, a flame might be initiated in gases which had been cooled to $-80°$ when the tube was heated strongly at one point. The length of time of exposure to a low temperature affects considerably the degree of dryness of the mixture, for Coehn and Tramm (*Ber.*, 1921, **54**, 1148) have shown

that a mixture dried by short exposure to the temperature of solid carbon dioxide and alcohol will inflame and burn quietly, although it will not "explode"; with a longer exposure to the low temperature a flame will not spread from the spark. It is, therefore, evident that an extremely small amount of water vapour is sufficient to promote slow burning. Payman and Wheeler (J., 1923, **123**, 1251) state that, although only a trace of moisture is needed to enable the propagation of flame to take place, about 6% is required to give the flame its complete freedom. Bone, Fraser, and Newitt (*Proc. Roy. Soc.*, 1926, **110**, 640) believe that "whilst the presence of water vapour is undoubtedly helpful, it is not essential to the ignition and explosive combination of carbon monoxide and oxygen mixtures, but that, on the contrary, these gases can, and under high pressures do, combine directly."

In all the experiments quoted, the inflammation of the carbon monoxide mixture was effected by a spark, whereas in the present experiments ignition was by the detonation-wave of electrolytic gas; the results in the two cases are, however, in general agreement. When the carbon monoxide had a partial aqueous vapour pressure of 16 mm. (above 2% of moisture), the rate of explosion soon after ignition was between 700 and 800 m./sec., *i.e.*, about half the theoretical rate. Acceleration to detonation occurred at a considerable distance along the tube. Reduction of the pressure of aqueous vapour to 1 mm. or less had little effect upon either the extent of the retardation or the rate of acceleration of the slow flame. A further reduction in the moisture content had the effect of causing the flame to travel slowly over a greater distance; the flame, however, was never extinguished with the most complete drying we were able to effect.

The Addition of Hydrogen to $2CO + O_2$ (*moist and dried gases*).

A series of experiments has been carried out in which definite amounts of hydrogen, together with the equivalent amounts of oxygen, were added to carbon monoxide–oxygen mixtures, some of which were saturated at the ordinary temperatures with water vapour, whilst others were dried by method A (*vide supra*). The results of these experiments are detailed in Table III. In experiments with both wet and dried gases when the amount of hydrogen in the mixture did not exceed 0·7% the flame speed fell considerably, but when there was above 1·8% of hydrogen no fall occurred. Between these extremes the results were not consistent; even when the same mixture was used, the gases and the tube being dried by the same method, two results agreed but differed from a

TABLE III.

The effect of the addition of hydrogen to $2CO + O_2$.

Expt. No.	Length of tube.	% H_2.	Dried.	Wet.
293	135 cm.	0·6	Fall.	
294	135	0·6	,,	
295	135	0·6	,,	
296	135	0·6		Fall.
334	105	0·7		,,
259	98	0·7	Fall.	
291	135	0·9	,,	
292	135	0·9	No fall.	
232	88	1·1		No fall.
236	88	1·1		,,
262	98	1·2	Fall.	
332	60	1·2		No fall.
333	60	1·2		,,
288	143	1·3	No fall.	
289	135	1·3	Fall.	
290	135	1·3	No fall.	
245	166	1·5	Fall.	
246	160	1·5	,,	
286	143	1·8	No fall.	
287	143	2·3	,,	
233	88	2·5		No fall.
335	105	2·5		,,
336	105	2·5		,,
237	86	3·4		,,
231	88	4·2		,,
229	100	9·0		,,

third (Expts. 288—290). We can only believe that the ignition of mixtures which contain about 1% of hydrogen is largely affected by a very small difference in moisture content. In all the experiments with hydrogen, one of two results was always obtained: (i) the flame velocity was considerably decreased, usually to about 800 m./sec., or (ii) the flame velocity was high and became constant at about 1750 m./sec. soon after entering the carbon monoxide portion. Curve II (Fig. 5) illustrates the latter result. The slow flame in the mixture containing 0·9% of hydrogen is shown in Fig. 10, and the rapid flame (the explosion-wave) in the mixture containing 1·3% in Fig. 11.* When the slow flame was photographed further along the experimental tube, acceleration was seen to have taken place, and it appears to be certain that in these experiments (as in those without hydrogen) detonation would have ultimately occurred. The flames in several experiments were photographed at 135 cm. and the highest velocity recorded there was 1230 m./sec.

Continuous propagation of the explosion-wave immediately on ignition was given in a dried carbon monoxide mixture which

* The burning gases behind the wave front in Fig. 11 show marked horizontal bands; a discussion of this appearance will be given in a later communication.

contained 0·9% of hydrogen, but the damping down of the wave occurred in a mixture free from hydrogen but containing 2% of water vapour; hydrogen is thus more efficient than water vapour in allowing the explosion-wave to develop in the carbon monoxide–oxygen mixtures under these special conditions of ignition.

The explanation advanced by Dixon and Walls (*loc. cit.*, p. 1031) of the temporary damping down of the explosion-wave is based on the assumption that carbon dioxide is largely dissociated at the high temperature produced by the burning electrolytic gas; under those conditions, "the oxidation of the carbon monoxide might be too slow to maintain the explosion-wave." Their results led to the suggestion that as carbon monoxide was gradually replaced by more hydrogen in the mixed gases, the discontinuity would grow less and finally disappear. We have been unable to detect any gradual change in the appearance of the discontinuity; a very small change in the hydrogen content of a mixture changes the character of the ignition completely and we find it difficult to believe that the temperatures in the two instances where the amounts of hydrogen differ by, say, 0·2% can be sufficiently different to affect the degree of dissociation to any considerable extent. Since the behaviour of the carbon monoxide mixtures appears to depend upon the pressure and temperature conditions in the wave-front of the igniting mixture, experiments with various igniting mixtures are being carried out.

It has been suggested (Crussard, *Bull. Soc. Ind. Min.*, 1907, **6**, 257) that the explosion-wave consists of a shock-wave accompanied and sustained by a chemical reaction in the form of flame and that the normal propagation of the wave depends upon the mutual assistance provided by these two factors. It would appear that when carbon monoxide–oxygen mixtures are ignited by electrolytic gas, the concussion component from the primary mixture becomes separated from the inflammation; the latter becomes very much reduced in speed and the shock-wave travels away in front, also at a falling speed, since it is unsustained. The retarded flame then accelerates in the same way as when such a mixture is ignited from a spark, and eventually overtakes the retarded shock-wave, the second smaller check to the flame probably occurring at this point; the initiation of separate flames in front of the retarded flame appears to be caused by a mechanical wave which was preceding the latter at a short distance.

Summary.

An apparatus has been described by which a flame is photographed as it travels from one explosive gaseous mixture into another.

When the igniting and the ignited gases are mixtures of hydrogen and oxygen in different proportions, the flame travels in both mixtures at the normal explosion-wave rates, the velocity in the second mixture becoming adjusted within a few centimetres. When carbon monoxide–oxygen mixtures are ignited by electrolytic gas, the flame velocity falls rapidly to less than half the normal rate and detonation is re-established only after the flame has travelled several metres. A fairly complete drying of the carbon monoxide does not appear to decrease the flame speed below a certain limit although it lengthens the period before detonation. The addition of more than 1% of hydrogen to the carbon monoxide mixture allows the flame to proceed immediately at its full rate. A flame just previous to the setting up of the explosion-wave in these mixtures tends to show marked discontinuities.

In conclusion, we wish to express our indebtedness to the Chemical Society for grants towards the cost of photographic materials and to the Brunner–Mond Research Fund for apparatus. We desire to thank Mr. A. G. Hartley, M.Sc., for considerable help in the experimental portion of the paper, and Professor Dixon for his kindly interest and criticism.

THE UNIVERSITY, MANCHESTER. [*Received, August 23rd,* 1926.]

CCCCII.—*The Conductivity of Phosphoric Acid Solutions at* 0°.

By ALAN NEWTON CAMPBELL.

ALTHOUGH the conductivities of phosphoric acid solutions at 18° have been determined by Kohlrausch (Landolt-Börnstein, "Physikalisch-chemische Tabellen," 1912, p. 1100), those at 0° have not hitherto been investigated. It is stated by Partington (Taylor's "Treatise on Physical Chemistry," I, p. 538) that the conductivity of phosphoric acid solution has a negative temperature coefficient, but a very considerable decrease of conductivity from 18° to 0° has now been observed; presumably the statement of Partington refers, therefore, to higher temperatures.

All the usual precautions were taken, including calibration of the bridge, and the water used in making up the solutions was thrice distilled: (*a*) from potassium permanganate, (*b*) from baryta, (*c*) through a block-tin condenser. Water of this high degree of purity, however, was not strictly necessary in view of the high conductivity of the solutions. The phosphoric acid used was

B.D.H. "Analytical Reagent" (d 1·75); it contained 85·49% H_3PO_4, and was without reducing action on permanganate. The concentrations of the solutions were estimated volumetrically by Thomson's method (Sutton, "Volumetric Analysis," 1904, p. 113). An ordinary medical coil was used as the source of current. The values given were the means of several determinations in each case, and were reproducible within 1 mm. on a metre bridge.

In the table, p is the weight of anhydrous phosphoric acid per 100 g. of solution, n is the number of g.-mols. of phosphoric acid per 1000 g. of water, and κ is the specific conductivity. If the values for concentration and conductivity are plotted, the maximum conductivity is obtained as 1408×10^{-4} mho, occurring at 45·16% H_3PO_4 ($n = 8{\cdot}4$).

p.	n.	$10^4\,\kappa_0$ in mhos.	$\frac{1}{\kappa_0}\cdot\left(\frac{d\kappa}{dt}\right)_9$.	p.	n.	$10^4\,\kappa_0$ in mhos.	$\frac{1}{\kappa_0}\cdot\left(\frac{d\kappa}{dt}\right)_9$.
8·93	1	441	—	43·81	7·95	1400	0·0268
16·40	2	731	0·0150	45·47	8·51	1408	0·0270
22·73	3	929	0·0210	47·14	9·10	1392	0·0283
28·18	4	1124	0·0214	48·76	9·71	1376	0·0289
32·91	5	1238	0·0241	49·49	10	1368	0·0291
37·04	6	1357	0·0234	51·66	11	1342	0·0289
40·70	7	1374	0·0264	54·06	12	1314	0·0290
41·77	7·32	1396	0·0251				

The values of $1/\kappa_0 \cdot (d\kappa/dt)_9$ are obtained from Kohlrausch's series at 18° and the author's at 0°. It will be observed that they are much larger than Kohlrausch's values for $1/\kappa_{18} \cdot (d\kappa/dt)_{22}$ at corresponding concentrations. The temperature coefficient is therefore decreasing with increase of temperature and will eventually become negative in accordance with the statement of Partington (*loc. cit.*).

Summary.

1. The specific conductivities of phosphoric acid solutions at 0° have been determined over a wide range of concentrations, and the maximum conductivity has been evaluated.

2. The temperature coefficients are calculated and it is shown that these will eventually become negative.

UNIVERSITY OF ABERDEEN. [*Received, August 18th*, 1926.]

CCCCIII.—*Interaction between Hydrated Silica and Neutral Electrolytes in its Relation to the Nature of Hydrolytic Adsorption.*

By JNANENDRA NATH MUKHERJEE, BIVAS CHANDRA GHOSH, K. KRISHNAMURTI, GAJENDRA NARAYAN GHOSH, SUBHENDU KUMAR MITRA, and BANKIM CHANDRA ROY.

THE liberation of acids by the action of a neutral solution of a salt on silica is commonly represented as follows (compare Mellor, "Quantitative Inorganic Analysis," London, 1913, p. 172; Joseph and Hancock, J., 1923, **123**, 2022):

$$2n\mathrm{KCl} + \mathrm{H}_{2n}\mathrm{SiO}_{n+2} \rightleftharpoons 2n\mathrm{HCl} + \mathrm{K}_{2n}\mathrm{SiO}_{n+2} \quad . \quad (1)$$

So long as the two pure solid phases coexist at a given temperature, (*a*) the activity of the liberated hydrogen ions in the solution ought to be proportional to that of the potassium ions, and (*b*) if definite concentrations of salts of different cations are compared, the lower the solubility of the corresponding silicate the higher will be the activity of the hydrogen ions necessary to maintain ionic equilibrium with the insoluble acid (Nernst, "Theoretische Chemie," 1921, pp. 615—618; Noyes and Kohr, *Z. physikal. Chem.*, 1902, **42**, 336; Lewis and Randall, "Text Book of Thermodynamics," 1923, p. 482). We now show that the relationship stated in (*a*) does not hold good, and it must be assumed that the solid phase consists of some sort of solid solution of the so-called acid and insoluble salt. Similar cases have been discussed by Küster (*Z. anorg. Chem.*, 1899, **19**, 81).

We consider that the liberation of acids in the present instance is the result of displacement of hydrogen ions in the double layer by cations adsorbed from the solution (Mukherjee, *J. Indian Chem. Soc.*, 1925, **2**, 191; *Phil. Mag.*, 1922, **44**, 321).

EXPERIMENTAL.

As the purity of the silica used in the preliminary portion of this work has been disputed (Joseph and Hancock, *loc. cit.*), hydrated silica obtained from the hydrolysis in transparent silica vessels of doubly distilled silicon tetrachloride was used throughout the present work.* After being washed free from acid the silica was

* The silica could never have come in contact with free alkali, as it was obtained by washing out the acid with pure water until the p_H rose to 6·2—6·4. Unless otherwise stated, the silica was not washed further and it retained a slight amount of acid which could be removed by further washing so that the resistance of the wash water rose to the same value as that of the water used.

air-dried at the ordinary temperature in a place free from fumes. The different samples contained 60—90% of water of hydration.

Resistance glass vessels were used, experiments with transparent fused silica vessels having shown that no extraneous sources of error were thereby introduced. The purity of the water employed was always tested before use. Clark and Lubs's indicators and standards were used. The concentrations of electrolytes added to silica as given below are those of the original solution.

The Equilibrium Concentration of Hydrogen Ions in Contact with a Definite Concentration of Potassium Chloride.

To 14 g. of silica (80% hydration) in a clean transparent silica flask a definite volume of neutral (p_H 6·4—6·6) potassium chloride solution, saturated at room temperature (29—30°), was added, and after a definite interval of time a measured volume of the clear supernatant liquid was decanted and its p_H tested by indicators. A fresh portion of the potassium chloride solution was added and the process repeated. The results are given in Table I.

TABLE I.

Days.	p_H of KCl extract.	C.c. of sol. extracted.	Days.	p_H of KCl extract.	C.c. of sol. extracted	Days.	p_H of KCl extract.	C.c. of sol. extracted.
—	4·2	50	12	5·2	200	28	6·0	100
1	4·4	50	14	5·4	200	29	6·4	100
2	4·4	25	15	5·4	150	31	6·4	100
2	4·6	50	16	5·5	200	33	6·2	100
5	4·6	25	19	5·7	200	34	6·2	100
5	4·8	75	20	5·7	100	35	6·2	100
6	4·8	50	21	5·8	100	36	6·3	100
8	4·8	100	22	5·8	100	37	6·5	100
8	5·0	100	26	6·0	100	38	6·4	100
9	5·1	300	27	6·0	100	39	6·5	100

From these results, the total amount of acid liberated is calculated to be equivalent to $1·63 \times 10^{-5}$ g.-atom of hydrogen. The composition of the hydrated silica is 13·3 g.-mols. of water per g.-mol. of silicon dioxide. Of these 26·6 g.-atoms of hydrogen, only $3·5 \times 10^{-4}$ g.-atom has been replaced. Table I shows that, instead of a constant equilibrium concentration of hydrogen ions and a sudden fall, there is a gradual diminution until a solid residue is obtained which does not change the p_H of the potassium chloride solution even during 4 days' contact.

That all the replaceable hydrogen ions have not yet been removed is evident from the following experiments : 10 g. of silica (hydration 70%) were washed repeatedly as above with *N*-barium chloride solution (p_H 6·4) until the p_H of the extract showed no change. The clear supernatant solution was removed as far as possible by means

of a pipette and 50 c.c. of saturated barium chloride solution were added. The p_H of the supernatant solution fell to 5·8. The solution was removed once more and 50 c.c. of sodium nitrate solution, saturated at room temperature (p_H 6·4), were added. The p_H now fell to 4·8. In Table II are shown the total amounts of acid liberated by different cations until no more hydrogen ions are set free. It is seen that the capacity of the cations to liberate acids on continued washing is in the order $K^{\cdot} > Na^{\cdot} > Ba^{\cdot\cdot}$ in molar solution; also that the total amount of acid liberated depends on the concentration of the cation.

TABLE II.

	N-KCl.	*N*-NaCl.	*N*-$BaCl_2$.	2*N*-$BaCl_2$.	Sat. $BaCl_2$.*	Sat. $NaNO_3$.*
G.-ions of $H^{\cdot}$ liberated ($\times 10^4$)	0·3	0·2	0·15	0·15	0·34	0·56
G.-ions of $H^{\cdot}$ per g.-mol. of SiO_2 ($\times 10^4$)	6	4	3	3	6	10

* A different sample, with 66·15% water of hydration, was used in these experiments.

The solubility relationships which should be satisfied if our usual conceptions of such equilibria are valid for this case must now be considered.

Let S_A be the solubility of the "pure" acid (uncontaminated by its salts) in g.-mols. per litre, and S_K that of the corresponding "pure" potassium salt. In view of the weak character of silicic acid and its probable solubility, we shall assume that only the first-stage dissociation need be taken into account, especially as we are dealing with acidic solutions. The solubility in water of the acid or of the salt is a function of the composition of the solid solution, *i.e.*, the product of the respective molar fraction (expressed in terms of simple molecular weights of the acid and of the salt *) multiplied by the solubility of the pure substance. For the acid, the ionic product must be a constant depending on the temperature and composition of the solid solution and will be given by

$$C_{H^{\cdot}} \times C_{A'} = \{f(1-x) \,.\, S_A \alpha(1-x)\}^2 \,. \quad . \quad . \quad (2) \,\dagger$$

where $C_{H^{\cdot}}$ and $C_{A'}$ denote respectively the gram-ionic concentrations (or rather activities) of the hydrogen ion and the anion of the silicic acid in the solution; $(1-x)$ is equal to the fraction of the acid remaining unchanged; $f(1-x) \,.\, S_A$ is the solubility of the acid under these conditions; α is the theoretical degree of dissociation of the acid in a solution saturated with reference to the acid only in the solid

* For the barium salt the molar fraction will be $(1-x/2)$ for the acid and $x/2$ for the salt, assuming x to be small.

† The validity of this and the following equations is considered in the "Discussion."

solution, *i.e.*, assuming that the silicate is not passing into the solution, so that $C_{H^\cdot} = C_{A'}$. Actually $C_{H^\cdot} > C_{A'}$, but for equilibrium the ionic product $C_{H^\cdot} \times C_{A'}$, which in these dilute solutions measures the activity, must have a constant value determined by the above expression.

Similarly, putting $\alpha = 1$ for the salts, we have

$$C_{K^\cdot} \times C_{A'} = \{f(x) \,.\, S_K\}^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$C_{Ba^{\cdot\cdot}} \times C^2_{A'} = 4\{f(x/2) \,.\, S_{Ba}\}^3 \quad . \quad . \quad . \quad . \quad (4)$$

whence

$$C_{H^\cdot} = C_{K^\cdot}\{f(1-x) \,.\, S_A\alpha(1-x)\}^2/\{f(x) \,.\, S_K\}^2 \quad . \quad . \quad . \quad (5)$$

and

$$C_{H^\cdot} = C_{Ba^{\cdot\cdot}}{}^{1/2}\{f(1-x/2) \,.\, S_A\alpha(1-x/2)\}^2/2\{f(x/2) \,.\, S_{Ba}\}^{3/2} \quad (6)$$

The decrease in the concentration of hydrogen ions is to be explained by a gradual increase in the value of x.

The Concentration of Hydrogen Ions in Contact with Different Salts.

To 40 c.c. of each of a number of salt solutions contained in resistance-glass bottles were added 5 g. of silica. The hydrogen-ion concentration of the clear upper liquid as shown in Table III was determined after 24 hours from *E.M.F.* measurements, using normal calomel electrodes; the measurements were correct to $\pm 0{\cdot}5$ millivolt.

TABLE III.

Conc. (g.-mol. per litre).	(SiO_2, 41·1%; H_2O, 58·9%.) KCl.		(SiO_2, 39·0%; H_2O, 61·0%.) NaCl.		$BaCl_2$.	
	$p_{H^\cdot}$.	$C_{H^\cdot} \times 10^6$.	$p_{H^\cdot}$.	$C_{H^\cdot} \times 10^6$.	$p_{H^\cdot}$.	$C_{H^\cdot} \times 10^6$.
1	4·54	28·8	4·6	25	—	—
0·5	—	—	—	—	4·56	27·6
0·04	4·71	19·5	4·76	17·4	—	—
0·02	4·72	19·0	5·20	6·31	4·76	17·4
0·01	5·03	9·33	5·42	3·80	5·06	8·71
0·004	5·17	6·76	5·75	1·78	—	—
0·002	5·52	3·02	6·05	0·89	—	—
0·001	5·57	2·69	—	—	—	—

The relative effects of barium, calcium, potassium, and sodium chlorides were determined in strictly comparable experiments with a different sample of silica (hydration 62%). The results are given below. As before, the hydrogen-ion concentrations were determined from *E.M.F.* measurements.

TABLE III (*a*).

Electrolyte and concentration.	*M*.		0·01*M*.		0·002*M*.	
	$C_{H^\cdot} \times 10^6$.	$p_{H^\cdot}$.	$C_{H^\cdot} \times 10^6$.	$p_{H^\cdot}$.	$C_{H^\cdot} \times 10^6$.	$p_{H^\cdot}$.
$BaCl_2$	56·2	4·25	15·1	4·82	3·09	5·51
$CaCl_2$	49·9	4·31	8·91	5·05	1·74	5·76
KCl	39·8	4·40	5·62	5·25	1·22	5·95
NaCl	35·5	4·45	4·73	5·39	0·725	6·14

The relative effects of calcium and barium chlorides, being of special interest, were studied simultaneously and the data are given in Table IV. The silica contained 89·7% of water.

TABLE IV.

		Concentration of electrolyte.					
		0·05*M*.	0·01*M*.	0·005*M*.	0·002*M*.	0·001*M*.	0·0005*M*.
$BaCl_2$	$C_{H^+} \times 10^6$	28·8	7·18	5·62	4·20	3·12	2·45
	p_H	4·54	5·144	5·25	5·377	5·506	5·615
$CaCl_2$	$C_{H^+} \times 10^6$	22·0	4·41	3·49	2·44	1·66	1·10
	p_H	4·657	5·356	5·457	5·613	5·779	5·94

From the chemical point of view, the above results signify that the solubilities of the sodium and calcium salts are respectively greater than those of the potassium and barium salts, whereas actually calcium silicate is less soluble than the barium salt (Joseph and Oakley, J., 1925, **127**, 2816). On comparing the relative effects of these cations we find that at the higher concentrations individual differences tend to disappear. The only way to surmount this difficulty would be to assume, either that a calcium salt of some complex acid is formed which is more soluble than the corresponding barium salt, or that the relative solubilities of the calcium and barium salts in a state of solid solution have no relation to their relative solubilities in the pure state.

Moreover, in the experiment on the determination of the total quantity of acid liberated by repeated washing, potassium and barium solutions at a molar concentration had practically the same hydrogen-ion concentration initially (p_H 4·2 and 4·6, respectively) as determined with indicators. At the close of the washing, the p_H was 6·4 for both. Reference to the equations shows that this can only be explained by assuming that the solubility of the barium salt in a state of solid solution increases relatively much more rapidly with its percentage composition than that of the potassium salt. The same remark applies to the sodium salt. Thus at each stage we have to introduce *ad hoc* assumptions of changes in solubility.

The Effect of Electrolytes on the Electrical Charge of the Surface.

Electro-osmotic experiments were carried out in a modified form of the apparatus used by Briggs (*Nature*, 1922, **109**, Dec. 2). As there are inherent defects in this method of measurement, the results are only comparative. The electrodes were always connected to the main (220 volts) circuit, and their relative positions were fixed. The measurements were made at room temperature (29—30°), and are reproducible to within 6%. The figures given in Tables V, VI, and VII indicate the movement of the bubble in cm. per 3 minutes.

TABLE V.

Electrolyte.	Concentration (g.-mols. per 1000 litres). 0.	0·1.	0·16.	0·2.	0·25.	0·33.	0·5.	1·0.	2·0.	8·0.
NaCl	3·2	—	—	5·7	—	6·0	—	3·5	3·1	—
KCl	3·2	—	—	5·6	5·3	5·1	4·0	2·8	2·2	1·0
$BaCl_2$	3·2	4·0	3·9	—	—	—	3·0	2·6	—	—
HCl	3·2	—	—	1·4	—	0·9	—	0·6	—	—

TABLE VI.

Electrolyte.	Concentration. 0.	0·0002*N*.	0·001*N*.	Electrolyte.	Concentration. 0.	0·0002*N*.	0·001*N*.
$(COOK)_2$	3·5	7·2	6·3	KBr	3·5	5·7	2·5
K_2SO_4	3·5	6·4	3·7	KNO_3	3·5	5·4	2·5
KCl	3·5	5·6	2·8				

TABLE VII.

Electrolyte.	10^3 × Concentration of electrolyte. 0.	0·2*N*.	0·33*N*.	0·5*N*.	1*N*.	2*N*.
$LiNO_3$	3·5	6·1	6·5	6·0	4·5	3·3
KNO_3	3·5	5·4	5·0	—	2·6	2·5
$RbNO_3$	3·5	4·3	3·5	—	2·9	2·2

From Tables V—VII we find that (1) chemically pure hydrated silica has a negative charge in contact with pure water; (2) the capacity of these univalent cations of decreasing the negative charge at higher concentrations shows that their order of adsorption is $H^{\cdot} > Rb^{\cdot} > K^{\cdot} > Na^{\cdot}$ (compare *J. Indian Chem. Soc.*, 1925, **2**, 204); (3) it appears that, taking into consideration its valency, the barium ion is weakly adsorbed; (4) the experiments with potassium salts of different acids (Table VI) leave no doubt that anions are primarily adsorbed, since different anions have different effects.

The weak adsorbability of barium may be referred, on the basis of electrical adsorption, to a large value of x in the equation $W = N_1N_2E^2/Dx$ [Faraday Society Discussion, October, 1920; equation (10)]; on this theory barium will still have a greater effect than calcium.

Adsorbability of the Cation and its Capacity to Liberate Hydrogen Ions.

In comparing the effect of a cation on the electrical charge of the surface of a solid with its capacity to set free hydrogen ions from the surface layer, we have to remember that, whereas the variation in the electrical charge depends on the relative amounts of cations and anions "fixed" on the surface, the liberated hydrogen ions may come either from the mobile sheet of the double layer or from the primary layer. On theoretical grounds, in considering the equilibrium concentration of hydrogen ions in the present instance,

we are mainly concerned with the displacement by cations of hydrogen ions from the mobile sheet of the double layer. If we compare the relative effects of these cations we find that the concentrations of hydrogen ions decrease in the order $Ba^{\cdot\cdot} > Ca^{\cdot\cdot} > K^{\cdot} > Na^{\cdot}$. In complete agreement with our theory, the order is the same as that indicated by mobility (K, $\frac{1}{2}$Ba, Na) and valency which should determine the number of g.-ions of hydrogen liberated by the cation. At high concentrations, as hydrogen ions in the double layer are increasingly replaced by cations, and as the number of anions *primarily* adsorbed does not change to any large extent at these concentrations, the effect of the adsorption of a further amount of the cation will produce a much greater change in the ratio between the cation and hydrogen ions present in the double layer than when a smaller number of cations are present in it. Since the equilibrium is between the ions in the double layer and those in the bulk of the solution, the ratio between the two ions must also increase rapidly in the latter. The rate at which the concentration of the hydrogen ions increases with the concentration of the cation will therefore rapidly decrease and individual differences between the different cations will also diminish, because at high concentrations the adsorption will tend to a limit, namely, that corresponding to the state when all the primarily adsorbed anions are " covered " by cations. It is evident that at higher concentrations the different cations will be in equilibrium with practically the same concentration of hydrogen ions. It is thus unnecessary to introduce assumptions regarding changes in solubility, especially as we might doubt whether a solid solution of silica is really formed under the conditions of the experiments. The total quantities of acid liberated also show a similar effect of the concentration and adsorbability of the cation.

The Dependence of the Concentration of Hydrogen Ions on the Amount of Silica used.

If one changes the ratio of the weight of silica to the volume of solution—the amount of potassium chloride remaining constant—it is obvious that the extent of interchange between the hydrogen and potassium ions will be different. Consequently the ratio of the concentration of potassium to hydrogen ions should also vary. One of us (Mukherjee, Faraday Society Discussion, *loc. cit.*), in discussing the effect of a cation on the negative charge of the surface, considered the simplest case in which the following conditions were satisfied: (*a*) The number of primarily adsorbed ions per unit surface and their nature do not change; (*b*) there is only one kind of cation in the solution and in the double layer.

Apparently these conditions do not hold good in the present

instance, where two kinds of cation and more than one type of adsorbable anion are present. Experiments with different quantities of silica (see Table VIII) illustrate the relationship existing between the ratios of the cations in the double layer and in the solution.

TABLE VIII.

(Electrolyte, 50 c.c. of *N*-KCl. Hydration of silica, 89·7%.)

Wt. of silica.	$C_{H\cdot} \times 10^5$.	G.-atoms of K adsorbed per 10^5 g. of hydrated SiO_2.	G.-atoms of K adsorbed per 10^5 mol. of SiO_2.	$C_{K\cdot}/C_{H\cdot}$ (corrected for H_2O of hydration).
1 g.	3·1	0·158	92·1	$0·32 \times 10^5$
2 ,,	3·59	0·092	27·1	$0·27 \times 10^5$
4 ,,	4·82	0·062	9·3	$0·19 \times 10^5$
8 ,,	8·32	0·059	4·3	$0·106 \times 10^5$

It will be seen from col. 3 that the amount of potassium per g. of silica diminishes with increasing quantities of silica; also that the amount of potassium taken up by the solid is not proportional to the weight of the solid used (compare Joseph and Oakley, *loc. cit.*). As the amount of potassium adsorbed is very small compared with the total amount present, the concentration of the potassium ions is not materially altered by adsorption. Col. 5 gives the ratio of concentration of potassium to hydrogen ions in the solution, showing that a decrease in the ratio of potassium to hydrogen ions in the double layer is attended by a simultaneous although smaller decrease in the ratio in the solution. The higher concentration of hydrogen ions in the solution requires for equilibrium a relative increase in the number of hydrogen ions per unit surface of the double layer.

In conjunction with equation (5), these results signify that a decrease in the value of x increases the value of $C_{H\cdot}$. Assuming x to be small, $C_{H\cdot}$ should vary inversely as x^2 [putting $f(x) = x$]. Col. 2 shows that the rate of increase is much smaller than is required by this relationship. If x is not very small, then the divergence becomes still greater. As nothing is known regarding the manner in which the solubilities of the components of the solid solution change with the composition, a discussion of these results from the chemical point of view is unprofitable. From our point of view, it is easy to understand that a greater number of hydrogen ions in the double layer can only be in equilibrium with a higher concentration in solution.

The Adsorption of Acids by Silica.

The total amount of acid liberated on continued washing gives a rough indication of the amount of hydroxyl ions (covered or uncovered) adsorbed per g. of the substance. As the primary adsorption is attributed to chemical forces, other anions may also

be adsorbed. We have already seen from electro-osmotic experiments that anions are primarily adsorbed. The adsorption of anions is closely related to the adsorption of acids. A quantitative determination of the latter is of interest in relation to the acidity of clays. On chemical grounds, one would expect that the primary adsorption of hydroxyl ions would be very strong compared with that of other anions. The adsorption of acids should therefore be lower than that indicated by the total amount of acid liberated on continued washing. The adsorption of hydrochloric acid has been determined both by conductivity and by *E.M.F.* methods, corrections being applied for the diluting effect of the water of hydration. (It can also be demonstrated by the use of indicators.) In view of the method of preparation of the silica (p. 3023), the only possible extraneous source of alkali is ammonia from the air, but this was shown to be absent throughout. Great care was taken to shelter the samples from dust and fumes. The extremely low conductivity of the water in contact with silica shows that there are no electrolytic impurities.

TABLE IX.

Experiment A (Wt. of silica, 40 g.; hydration, 84·4%; vol. of solution, 100 c.c.).

Method.	Conc. of acid ($\times 10^4$). Before adsorption.	After adsorption.	Conc. of original acid (corrected for dilution by hydration) $\times 10^4$.	Change in conc. due to adsorption $\times 10^4$.	Amount adsorbed per g.-mol. of silicon dioxide $\times 10^4$.
Conductivity.*	9·6	6·85	7·22	0·37	0·47
E.M.F.	9·43	6·38	7·05	0·67	0·65

Experiment B (Wt. of silica, 20 g.; hydration, 59·6%; vol. of solution, 30 c.c.).

E.M.F.	2·82	0·43	2	1·97	0·62

Experiment C (Wt. of silica, 100 g.; hydration, 86·6%; vol. of solution, 100 c.c.).

Conductivity	3·05	1·46	1·93	0·47	0·5
E.M.F.	2·93	1	1·86	0·86	0·91

* For hydrochloric acid Λ_∞ has been taken as 455 at 30°.

We have found a difference in the amount adsorbed as calculated from *E.M.F.* and from conductivity measurements. The difference cannot be accounted for on the basis of replacement of hydrogen ion by another cation and, as no free alkali could possibly come in contact with the samples, we believe the *E.M.F.* to be less accurate than the conductivity measurements, especially as the hydrogen electrodes often lost their reproducibility. The liquid is never free from suspended particles, although in presence of neutral salt the upper liquid becomes perfectly clear after 24 hours.

The only impurity that could possibly be present in our silica is titanium oxide: the silicon tetrachloride employed (Merck or Kahlbaum) contained titanium chloride, but two distillations from a water-bath rendered it free from titanium as shown by the following analytical data, for which we are indebted to Mr. P. R. Ray, M.A.: (1) 8·8009 g. of hydrated silica were heated with hydrofluoric and sulphuric acids in a platinum basin. The latter gained 0·3 mg. in weight, of which 0·1 mg. was due to impurities in the acids, as shown by a control. The difference of 0·2 mg. is within the limits of experimental error. (2) 6 G. of ignited silica were fused with potassium bisulphate and extracted with water. Colorimetric comparisons, after the addition of hydrogen peroxide, showed this solution to contain less titanium than 0·04 c.c. of a solution containing 1 mg. of titanium per c.c., *i.e.*, the titanium, if any, is therefore less than 8×10^{-5} g.-atom per mol. of silicon dioxide, too little to account for the observed adsorption.

The results given above leave no doubt as to the adsorption of acid by silica, and the amount adsorbed, although small, is comparable with the acidity to be attributed to the silica itself.

Discussion.

We shall now briefly discuss some further difficulties in the way of applying our usual chemical conceptions to this reaction. It is well known that in the presence of an electrolyte with or without a common ion the solubility of the so-called undissociated molecules does not remain constant. The product of the ionic activities, however, is constant and independent of the concentration and nature of the ions present. Considerations based on the solubility of pure phases give no clue as to the activity of the hydrogen ion liberated in presence of different cations. Thus in equations (2) to (6) it is not sufficient to know the values of S_{A_1}, S_{B_2}, etc.: we must also know how the solubility (or activity) changes with the nature and concentration of the added electrolyte; *i.e.*, the function $f(1 - x)$ or $f(x)$ may vary from one electrolyte to another. As these equations in reality deal with thermodynamic quantities and not with solubilities, we have always to assume that the solubilities are such as would satisfy the thermodynamic relationships. Moreover, it is not at present possible to predict on theoretical grounds the solubilities of the different salts in such cases. On the contrary, from our point of view the capacity of a cation to liberate hydrogen ions depends upon its mobility and valency when the cation is not primarily adsorbed by the surface, and electrical forces alone are responsible for the adsorption.

Lastly, if we consider that at the same molar concentration the

activity coefficient of the bivalent cations is less than that of the univalent cations (Lewis and Randall, *loc. cit.*), it appears that the activity of the liberated hydrogen ions would be still greater for the bivalent cations than for univalent ions when their effects are compared at concentrations such that both have the same actual activity. The order $K^{\cdot} > Ba^{\cdot\cdot} > Na^{\cdot}$ is, however, theoretically possible if mobility alone determines the electrical adsorbability.

Summary.

(1) It is shown that the usual conceptions of chemical equilibrium fail to account for the interaction between silica and neutral salt solutions.

(2) In agreement with Mukherjee's theory, there is a close relationship between the valency and mobility of the cation and its effect on the liberation of hydrogen ions.

(3) The adsorption of acids by silica has been definitely demonstrated.

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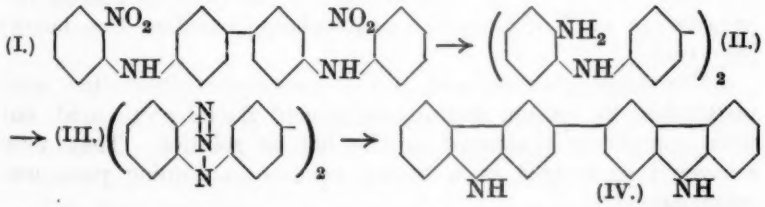
CALCUTTA. [*Received, July 7th*, 1926.]

CCCCIV.—*The Dicarbazyls. Part I. Synthesis of 3 : 3′-Dicarbazyl.*

By STANLEY HORWOOD TUCKER.

OXIDATION of carbazole gives rise to two dicarbazyls, m. p. 220° and 265°, respectively, and an amorphous substance (Perkin and Tucker, J., 1921, **119**, 216). Neither of these dicarbazyls is 3 : 3′-*dicarbazyl*, the synthesis of which has been achieved according to the scheme :



3 : 3′-Dicarbazyl was not formed in the oxidation of carbazole with potassium permanganate in acetone solution; and the amorphous substance obtained in 75% yield was not the product of oxidation of any 3 : 3′-dicarbazyl that might have been formed (compare the conversion of diphenylbenzidine into amorphous bisdiphenyldibiphenylenehydrazine; Wieland and Wecker, *Ber.*, 1922, **55**, 1804),

for 3 : 3′-dicarb zyl, on oxidation under similar conditions, gives a different amorphous substance.

3 : 3′-Dicarbazyl has also been prepared by the direct oxidation of carbazole in acid solution—a process that will be described in a future paper.

Experimental.

NN′-*Di*-o-*nitrophenylbenzidine* (I).—(Method A.) A mixture of benzidine (16 g.) and *o*-chloronitrobenzene (72 g.) was stirred for 3 hours in an oil-bath at 245° (compare Schöpff, *Ber.*, 1889, **22**, 904), the hot melt poured into benzene, and, when cold, the insoluble portion extracted with cold benzene. The dark brown, powdery residue (10—15 g.) was extracted thrice with boiling xylene (200 c.c. each time). The xylene extract was boiled with animal charcoal for ½ hour and concentrated to a very small bulk; the brick-red crystals which separated on cooling recrystallised from acetic anhydride in scarlet crystals (5 g.), m. p. 240° (Found: N, 13·0. $C_{24}H_{18}O_4N_4$ requires N, 13·1%).

(Method B.) A mixture of *o*-nitrodiphenylamine (3 g.), glacial acetic acid (200 c.c.), and concentrated sulphuric acid (50 c.c.) was cooled and slowly treated with a solution of sodium dichromate (3 g.) in water (5 c.c.) and glacial acetic acid (20 c.c.) (compare Wieland, *Ber.*, 1913, **46**, 3300). After ½ hour, the reddish-purple solution was poured into excess of sulphurous acid, the brown precipitate was extracted several times with boiling xylene (residue, 1 g.), and the extracts were concentrated, filtered from a brown impurity which separated, and evaporated almost to dryness. The red crystals thus obtained melted at 240° after recrystallisation from acetic anhydride. The yield (1 g.) was slightly reduced when the quantities of acetic and sulphuric acids were halved.

The identity of the products obtained by methods A and B was established by the m. p. of a mixture of the two and also by the preparation of *NN′*-diacetyldi-*o*-nitrophenylbenzidine (see below) from each.

o-Nitrodiphenylamine and *NN′*-di-*o*-nitrophenylbenzidine were unattacked by sodium dichromate in cold glacial acetic acid, but were completely destroyed in the boiling solution. They were recovered unchanged from boiling acetone containing potassium permanganate.

NN′-*Di*-o-*nitrophenylbenzidine* is very sparingly soluble in glacial acetic acid or alcohol, more soluble in acetone, and very soluble in pyridine or benzaldehyde. It crystallises best from xylene or acetic anhydride.

N-o-*Nitrophenylbenzidine*.—The benzene extract mentioned above (method A) was steam-distilled, and the black residue boiled with

alcohol. The solution, after being filtered from a small quantity of *NN′*-di-*o*-nitrophenylbenzidine, deposited orange crystals which, after several recrystallisations, became dark crimson and finally reddish-orange, pointed laminæ of N-o-*nitrophenylbenzidine* (Found : N, 13·7. $C_{18}H_{15}O_2N_3$ requires N, 13·8%). The yield was considerably increased by carrying out the experiment at 235°, less *NN′*-di-*o*-nitrophenylbenzidine being formed.

N-*Acetyl*-N′-o-*nitrophenylbenzidine* was prepared by boiling *o*-nitrophenylbenzidine with excess of acetic anhydride for ½ hour; the liquid, after being concentrated to a very small bulk, deposited the *acetyl* derivative. This crystallised from glacial acetic acid in orange laminæ (Found : N, 12·0. $C_{20}H_{17}O_3N_3$ requires N, 12·1%), from anisole in reddish-orange leaflets, from alcohol or xylene as a mixture of yellowish-orange and reddish-orange leaflets, and from ethyl acetate, in which it was sparingly soluble, in yellowish-orange leaflets with a bronze reflex; the ethyl acetate mother-liquor slowly deposited thick rods. All these varieties, alone or in admixture, melted at 222° and there was no evidence that solvent of crystallisation was present. The substance was almost insoluble in carbon tetrachloride or methyl alcohol but readily soluble in chloroform.

NN′-*Diacetyl*-NN′-*di*-o-*nitrophenylbenzidine* was prepared by boiling *NN′*-di-*o*-nitrophenylbenzidine with excess of acetic anhydride containing a trace of concentrated sulphuric acid (unless this catalyst was present, no reaction occurred). The solution, the colour of which changed in a few minutes from scarlet to brown, was poured into water and the precipitate was crystallised from benzene with the aid of animal charcoal, straw-yellow, diamond-shaped laminæ being obtained, m. p. 80—85° (Found : N, 8·8. $C_{28}H_{22}O_6N_4,2C_6H_6$ requires N, 8·4%). The compound separated with one molecule of solvent of crystallisation from ethyl alcohol (m. p. 120° with effervescence), glacial acetic acid (m. p. 100—105°), and methyl alcohol, in which it was sparingly soluble after the first crystallisation (m. p. 125—130°). It was very soluble in acetone, pyridine, acetic anhydride, or hot anisole, almost insoluble in carbon tetrachloride, and separated as an oil from xylene and toluene; it crystallised in minute, lemon-yellow rods from ethyl acetate.

The diacetyl derivative prepared from *NN′*-di-*o*-nitrophenylbenzidine which had been obtained from *o*-nitrodiphenylamine (method B) separated from methyl alcohol in orange crystals; successive crystallisations from ethyl acetate and methyl alcohol then gave yellow crystals.

NN′-*Di*-o-*aminophenylbenzidine* (II).—*NN′*-Di-*o*-nitrophenylbenzidine (10 g.), alcohol (250 c.c.), concentrated hydrochloric acid

(250 c.c.), and excess of tin were vigorously boiled together until the red colour changed to a faint brown (3—4 hours). The crystalline mixture obtained on cooling was separated and extracted with hot dilute hydrochloric acid and the hot extract was poured into a hot concentrated solution of caustic soda. The precipitate obtained, after being dried, crystallised from benzene, in which it was sparingly soluble, in nacreous, white plates of NN'-*di*-o-*aminophenylbenzidine*, which shrank at 205° and melted to a faintly brown liquid at 218° (yield, 60—70%) (Found: C, 78·4; H, 5·9; N, 15·3. $C_{24}H_{22}N_4$ requires C, 78·7; H, 6·0; N, 15·3%). The base is sparingly soluble in alcohol, and very soluble in acetone, *cyclo*hexanone, or pyridine, and is partly adsorbed from the solutions by animal charcoal; it is insoluble in carbon tetrachloride. It dissolves in cold glacial acetic acid and in acetic anhydride, and the solutions immediately deposit needles and prisms respectively; the reactions involved will be considered in a later paper.

The *dihydrochloride* crystallises from very dilute hydrochloric acid in cream-coloured needles arranged in fish-bone fashion and becomes green to blue at 230—260° (Found: Cl, 15·9. $C_{24}H_{22}N_4,2HCl$ requires Cl, 16·2%). It readily dissociates, even in boiling dilute hydrochloric acid, the base separating as a salmon-pink powder.

NN'-Di-*o*-nitrophenylbenzidine in boiling glacial acetic acid solution was readily reduced by zinc dust. This method was not adopted, however, because prolonged boiling with glacial acetic acid converted the diamino-compound produced into a benziminazole. The reaction is being studied.

4 : 4'-*Di*-1'' : 2'' : 3''-*benztriazolyldiphenyl* (III).—*NN'*-Di-*o*-aminophenylbenzidine (5 g.), dissolved in hot glacial acetic acid (100 c.c.), was added all at once to cold glacial acetic acid (100 c.c.) and solid sodium nitrite (10 g.). A pale brown, flocculent precipitate separated from the vigorously effervescing, red liquid. The mixture was boiled for a minute, and filtered while warm. The precipitate, after being washed with cold glacial acetic acid and with water, was boiled with acetic anhydride (about 1 l.) and animal charcoal for ½ hour; thereafter the product was obtained in cream-coloured micro-laminæ which shrank at 295° and melted at 299° with darkening but no effervescence (yield, 4·2 g.; 80%) (Found: N, 21·6. $C_{24}H_{16}N_6$ requires N, 21·6%). It is very soluble in hot benzaldehyde, pyridine, or nitrobenzene, sparingly soluble in anisole, and almost insoluble in glacial acetic acid, alcohol, acetone, carbon tetrachloride, amyl alcohol, xylene, or ethyl acetate. The colourless solution in concentrated sulphuric acid becomes mauve on the addition of a trace of nitric acid.

Diazotisation of *NN'*-di-*o*-aminophenylbenzidine with amyl

nitrite in glacial acetic acid gave an impure product; and treatment of the amine hydrochloride in excess of hydrochloric acid with sodium or potassium nitrite solution gave deep mauve products from which it was difficult to isolate any of the desired benztriazole.

3 : 3′-*Dicarbazyl* (IV).—The preceding benztriazole derivative (4 g.) in 2 g. lots was very carefully heated over a free flame for a few minutes until it had melted and the gentle effervescence that set in had ceased. (The liquid explodes if it is overheated.) The black residue dissolved completely in anisole * (about 500 c.c.). The solution was boiled for 5 minutes with animal charcoal and filtered; the pale yellow filtrate deposited 3 : 3′-*dicarbazyl* (1·7 g.; yield, about 50%) as a colourless, microcrystalline powder (Found : C, 86·4; H, 4·7; N, 8·7. $C_{24}H_{16}N_2$ requires C, 86·7; H, 4·8; N, 8·4%).

If the decomposition of the dibenztriazolyldiphenyl has been incomplete, the filtrate from the charcoal first deposits the unchanged material as feathery crystals.

3 : 3′-Dicarbazyl melts above 350° without decomposition. It crystallises from benzaldehyde with considerable loss and from nitrobenzene, aniline, or tetrahydronaphthalene in an impure condition. It is insoluble in alcohol, carbon tetrachloride, or trichloroethylene, slightly soluble in acetone, amyl alcohol, xylene, or acetic anhydride, more soluble in methyl ethyl ketone, and readily soluble in *cyclo*hexanone or pyridine; the concentrated solutions deposit amorphous material. Mixed solvents also are ineffectual for crystallisation. 3 : 3′ -Dicarbazyl is insoluble in camphor, acetic acid, bromoform, benzene, naphthalene, and other solvents used for determining molecular weights. It dissolves in cold concentrated sulphuric acid; the emerald-green solution becomes ink-blue on addition of a trace of nitric acid—a reaction characteristic of carbazoles. 3 : 3′-Dicarbazyl distils at a red heat, subliming in small quantity in long, rectangular laminæ, and the vapour has a carbazole-like odour. It also resembles carbazole in having a faint violet fluorescence when quite pure.

3 : 3′-Dicarbazyl can be separated from dibenztriazolyldiphenyl by means of much acetone, in which the latter is insoluble.

Oxidation of 3 : 3′-*Dicarbazyl*.—A solution of 3 : 3′-dicarbazyl in acetone was boiled with excess of potassium permanganate for one hour. The brown precipitate was separated and warmed with sulphurous acid, and the yellow precipitate thus formed was washed with water and dried. The acetone filtrate gave similarly what seemed to be the same substance. The united amorphous products

* The anisole was washed with aqueous ammonia (*d* 0·880) to remove traces of sulphuric acid, which turn 3 : 3′-dicarbazyl green.

dried to a pale brown powder. This was boiled with acetic anhydride containing a trace of concentrated sulphuric acid to remove unchanged 3 : 3′-dicarbazyl, but it was completely insoluble. It was insoluble in benzene, xylene, acetone, acetic anhydride, acetic acid, alcohol, ether, or chloroform. It dissolved partly, leaving gelatinous residues, in nitrobenzene, anisole, tetrahydronaphthalene, pyridine, *cyclo*hexanone, and aniline. Solutions of the substance in the last three solvents were boiled with charcoal, filtered, and poured into acetone. The small amount of precipitate obtained was pale brown. It charred at a high temperature, contained a trace of sulphur, and left no residue when burnt in oxygen.

9 : 9′-*Diacetyl*-3 : 3′-*dicarbazyl*.—3 : 3′-Dicarbazyl dissolved gradually in excess of boiling acetic anhydride, but solution was effected at once by addition of a trace of concentrated sulphuric acid. The mixture was poured into water; the precipitate crystallised from glacial acetic acid in minute rosettes of colourless needles, m. p. 247—249° (Found : C, 80·6; H, 4·6; N, 6·7. *M*, by Rast's method, 425. $C_{28}H_{20}O_2N_2$ requires C, 80·8; H, 4·8; N, 6·7%; *M*, 416). It crystallised also from anisole and was readily soluble in acetic anhydride or cold pyridine, less soluble in acetone, xylene, toluene, or ethyl acetate, and insoluble in benzene, alcohol, or carbon tetrachloride. Hydrolysis was brought about in 1—2 hours by a boiling mixture of glacial acetic acid and dilute sulphuric or hydrochloric acid; 3 : 3′-dicarbazyl was slowly precipitated as a green or as a clean grey product according as sulphuric acid or hydrochloric acid was used.

I wish to thank Mr. James Cameron for repeating several of the analyses and preparing the initial nitro-compound in quantity.

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CCCCV.—*The Stereochemistry of the Hydronaphthalenes. Part I. Decahydro-β-naphthamides.*

By FRANCIS WILLIAM KAY and NOEL STUART.

MOHR'S theory of the isomerism of the decahydronaphthalenes, based on the views of Sachse on the strainless character of the *cyclo*hexane ring (*J. pr. Chem.*, 1918, **98**, 315), indicates that a monosubstituted decahydronaphthalene should exist in four distinct racemic forms. Decahydro-β-naphthoic acid, for example, should exist on this theory in the four racemic modifications represented diagrammatically by the formulæ I—IV, which show one

of the two enantiomeric components of each form. I and II are derivatives of *cis*-, III and IV of *trans*-decahydronaphthalene.

Borsche and Lange (*Annalen*, 1923, **434**, 219), by fractionally crystallising the amide, isolated two of the four racemic forms of decahydro-β-naphthoic acid, melting respectively at 165—166° and 195°. In a footnote, they hinted at the possible existence of a third racemic form, but they apparently failed to realise the stereochemical significance of their results.

The re-examination of decahydro-β-naphthoic acid by the present authors revealed the existence of a third isomeride in the form of an amide melting at 139—140° and indicated the occurrence of a fourth.

Decahydro-β-naphthamide was prepared by reducing *ar*-tetrahydro-β-naphthoic acid and applying the usual technique to the crude decahydro-acid thus obtained—fractional crystallisation of the amidic mixture was preferred, as the corresponding mixture of acids was oily. Reduction with amyl alcohol and sodium at 150° yielded almost solely a *trans*-decahydro-β-naphthamide, contrary to the effect of catalytic hydrogenation, which produces *cis*-decahydronaphthalene to the extent of 90% (Willstätter and Seitz, *Ber.*, 1924, **57**, 683). The hydrogenation of the naphthalene nucleus is in fact conditioned by temperature and other physical factors, for the use of ethyl alcohol in the reduction of the tetrahydro-acid gave a totally different result, exhaustive fractional crystallisation of the mixed amides yielding a sparingly soluble component with a maximum melting point of 169—171° and a more soluble one, m. p. 139—140°, constituting 66% of the mixture. Neither of these two amides has been previously isolated, and their existence must be regarded as confirming the stereochemical ideas elaborated above.

Experimental.

Decahydro-β-naphthoic Acids.—(1) *ar*-Tetrahydro-β-naphthoic acid (5 g.), dissolved in 150 c.c. of amyl alcohol, was dropped on to 20 g. of sodium (five times the theoretical quantity) heated at 150°; towards the end of the reaction 150 c.c. of amyl alcohol were added to dissolve the remaining sodium. The product was poured into

water, and the amyl alcohol removed by steam distillation. (It is not sufficient merely to distil the aqueous layer, as the sodium salt of the decahydro-acid is appreciably soluble in amyl alcohol.) The alkaline solution was acidified with dilute hydrochloric acid, the decahydro-acid separating as an oil which solidified to a waxy solid, m. p. 65—75°. (2) The above procedure was repeated, 100 c.c. of ethyl alcohol being used in place of the amyl alcohol and a further 50 c.c. added to dissolve all the sodium. The product solidified more rapidly than the preceding one and melted at 80—90°.

Decahydro-β-naphthamides.—A solution of 5 g. of the decahydro-acid in 50 c.c. of chloroform was dried over calcium chloride and treated with 7 g. of phosphorus pentachloride in the cold. When the evolution of hydrogen chloride ceased, the chloroform was distilled in a vacuum, and the residue evaporated several times with fresh chloroform to remove phosphorus oxychloride. The product was maintained for some time at 100° in a vacuum and was then slowly poured into 150 c.c. of concentrated aqueous ammonia; the crude amide, thus obtained in white flakes, melted, when dry, at 105—120° or 110—122° according as the initial acid had been prepared by reduction with amyl alcohol or with ethyl alcohol.

Fractionation of the Decahydro-β-naphthamides.—A solution of the crude amide in cold 50% aqueous alcohol was treated with successive small quantities of water; after each addition the solution was warmed slightly to dissolve the precipitated amide and then allowed to cool slowly and the crystals deposited were removed. In order to obtain the final, lower-melting and more water-soluble portions of the amide it was necessary to concentrate the solution. The fractions so obtained were further sub-divided in the same manner. Fractions having approximately the same m. p. were now combined and again fractionated. As a rule, the first crop obtained from any fraction had a higher m. p. than the last crop from the preceding fraction.

(1) *Amides from the acid obtained by reduction with amyl alcohol.* After four operations, an amide, m. p. 195—196°, and a small quantity of another, m. p. 171—174°, were obtained. By systematically working up the mother-liquors, almost all the 195°-amide was fractionated out in about twenty operations, leaving vanishingly small fractions with melting points between 100° and 195°.

(2) *Amides from the acid obtained by reduction with ethyl alcohol.* After eight operations, an amide of m. p. 169—171° was obtained (Found: N, 7·4. $C_{11}H_{19}ON$ requires N, 7·7%); exhaustive fractionation gave also, in twenty-four operations, an amide of m. p. 139—140° (Found: N, 7·5%) and scarcely anything else.

We desire to express our thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of us (N.S.) which enabled this research to be carried out.

UNIVERSITY OF LIVERPOOL. [*Received, February 23rd,* 1925.]

CCCCVI.—*The Interaction of Thiocarbonyl Chloride and Chloro-substituted Anilines and the Inhibitory Action of* ortho-*Substituents.*

By GEORGE MALCOLM DYSON, HERBERT JOHN GEORGE, and ROBERT FERGUS HUNTER.

THE formation of arylthiocarbimides by Hofmann's method (*Annalen*, 1846, **57**, 256) is greatly inhibited by the presence of one nuclear halogen atom in the aniline and almost completely inhibited by two; indeed the only dihalogenated arylthiocarbimides hitherto synthesised, *viz.*, 2 : 4-dichloro- and 2 : 4-dibromo-phenylthiocarbimides (Chattaway, Hardy, and Watts, J., 1924, **125**, 1552), were obtained with considerable difficulty by acid hydrolysis of the corresponding *s*-phenylarylthiocarbamides. These facts led the present authors to extend the synthesis of thiocarbimides by means of thiocarbonyl chloride (Rathke, *Ber.*, 1872, **5**, 799; Dyson and George, J., 1924, **125**, 1702; Dyson and Hunter, *J. Soc. Chem. Ind.*, 1926, **45**, 83T) to the chloro-substituted arylthiocarbimides.

The desired reaction proceeded readily with *m*-chloroaniline and even more readily with *p*-chloroaniline, sluggishly with *o*-chloroaniline, readily with 3 : 4- and 3 : 5-dichloroanilines, slowly with 2 : 4- and 2 : 5-dichloroanilines, and not at all with 2 : 6-dichloroaniline; evidently it is inhibited greatly by one *o*-chlorine atom and completely by two. In accordance with this deduction, 2 : 3 : 5 : 6-tetrachloroaniline and pentachloroaniline, and also 2 : 6-dibromo- and 2 : 4 : 6-tribromo-anilines, did not react with thiocarbonyl chloride.

Thiocarbonyl chloride reacted with 3 : 4 : 5- and with 3 : 4 : 6-trichloroaniline to give the corresponding trichlorophenylthiocarbimides—the first trihalogenated arylthiocarbimides to be isolated.

All the thiocarbimides synthesised in this work were characterised in the form of the corresponding thiocarbamides, which are well-defined, crystalline substances.

EXPERIMENTAL.

The thiocarbimides described below were prepared as follows: Thiocarbonyl chloride (1 mol.) was completely suspended in cold

water (10 vols.) by vigorous stirring during the addition of the chloroaniline (0·75 mol.), dissolved in chloroform (5 vols.). After ½ hour's stirring, the chloroform layer was removed and dried with calcium chloride and the solvent was evaporated on a steam-bath; the thiocarbimide was obtained by fractionally distilling the residual oil.

The chlorophenylthiocarbamides, $NHAr{\cdot}CS{\cdot}NH_2$, were prepared from the respective thiocarbimides and warm alcoholic ammonia, and the *s*-dichlorophenylthiocarbamides, $CS(NHAr)_2$, from the thiocarbimides (1 mol.) and the corresponding chloroanilines (1 mol.) in chloroform; they were usually crystallised from dilute alcohol.

The following compounds were prepared: *o*-Chlorophenylthiocarbimide, a pale yellow oil, b. p. 260—262°/760 mm., having a pungent odour and lachrymatory properties (Found: S, 18·9%). *o*-Chlorophenylthiocarbamide (prepared at 15°, since heating produces a brown tar which apparently contains *o*-aminophenylthiocarbamide), short needles, m. p. 146° (Found: S, 17·0%). *s*-Di-*o*-chlorophenylthiocarbamide, needles, m. p. 129° (Found: S, 11·1%).

m-Chlorophenylthiocarbimide, a colourless, highly refractive oil, b. p. 249—250°/760 mm., having a pungent odour (Found: S, 19·0%). *m*-Chlorophenylthiocarbamide, long, flat plates, m. p. 140° (Found: S, 17·1%). *s*-Di-*m*-chlorophenylthiocarbamide, small prisms, m. p. 131° (Found: S, 10·8%).

p-Chlorophenylthiocarbimide, broad, shining plates, m. p. 45°, having the odour of aniseed (Found: S, 18·6%). *p*-Chlorophenylthiocarbamide, broad, glistening plates, m. p. 174° (Found: S, 17·3%). *s*-Di-*p*-chlorophenylthiocarbamide, glistening needles, m. p. 176° (Found: S, 10·7%).

2 : 3-*Dichlorophenylthiocarbimide*, a highly refractive oil, b. p. 256—258°/760 mm. (Found: S, 16·0. $C_7H_3NCl_2S$ requires S, 15·7%). 2 : 3-*Dichlorophenylthiocarbamide*, needles, m. p. 148° (Found: S, 14·7. $C_7H_6N_2Cl_2S$ requires S, 14·5%). s-*Di*-2 : 3-*dichlorophenylthiocarbamide*, thin laminæ, m. p. 140° (Found: S, 8·8. $C_{13}H_8N_2Cl_4S$ requires S, 8·7%).

2 : 4-Dichlorophenylthiocarbimide, small prisms, m. p. 39·5°, b. p. 260°/760 mm., having the odour of aniseed (Found: S, 16·1%). 2 : 4-Dichlorophenylthiocarbamide, small crystals, m. p. 160° (Found: S, 14·4%). *s*-Di-2 : 4-dichlorophenylthiocarbamide, needles m. p. 169° (Found: S, 8·8%).

3 : 4-Dichlorophenylthiocarbimide, a pale yellow oil, b. p. 262°/760 mm., which solidified (Found: S, 15·7%). 3 : 4-Dichlorophenylthiocarbamide, needles, m. p. 164° (Found: S, 14·5%). *s*-Di-3 : 4-dichlorophenylthiocarbamide, large, broad plates, m. p. 144° (Found: S, 8·7%).

3 : 5-Dichlorophenylthiocarbimide, long needles, m. p. 45—50°, b. p. 274°/760 mm. (Found : S, 16·0%). 3 : 5-Dichlorophenylthiocarbamide, slender needles, m. p. 155° (Found : S, 14·4%). *s*-Di-3 : 5-dichlorophenylthiocarbamide, small prisms, m. p. 142° (Found : S, 7·1%).

3 : 4 : 5-*Trichlorophenylthiocarbimide*, an oil, b. p. 280° (decomp.). *s*-*Di*-3 : 4 : 5-*trichlorophenylthiocarbamide*, short needles, m. p. 140° (Found : S, 7·5. $C_{13}H_6N_2Cl_6S$ requires S, 7·3%).

3 : 4 : 6-*Trichlorophenylthiocarbimide*, an oil, b. p. 280°, which slowly solidified (Found : S, 14·0. $C_7H_2NCl_3S$ requires S, 13·4%). 3 : 4 : 6-*Trichlorophenylthiocarbamide*, needles, m. p. 162° (Found : S, 13·0. $C_7H_5N_2Cl_3S$ requires S, 13·4%).

2 : 6-*Dichloroaniline*.—Beilstein and Kurbatow's method (*Annalen*, 1879, **196**, 216) being unsatisfactory, this substance was prepared as follows (compare Heinichen, *Annalen*, 1889, **253**, 275; Orton and Pearson, J., 1908, **93**, 735) : A neutral solution of sulphanilic acid (1 mol.) in 25% aqueous sodium hydroxide was diluted until the concentration of sulphanilic acid was approximately 1%, and into it, cooled in ice, the calculated quantity of chlorine diluted with carbon dioxide (10 vols.) was passed. The crude 2 : 6-dichlorosulphanilic acid obtained by evaporating the filtered solution after treatment with animal charcoal was mixed with 98% sulphuric acid (10 parts) and treated with steam at 180°. The 2 : 6-dichloroaniline that distilled crystallised from dilute alcohol in slender needles, m. p. 39° (yield, 15—20%). It was recovered unchanged after being heated with thiocarbonyl chloride in a sealed tube at 180—200°.

3 : 5-*Dichloroaniline*.—*s*-Trinitrobenzene in alcoholic solution was reduced with ammonium sulphide and the 3 : 5-dinitroaniline produced was diazotised and boiled with a solution of cuprous chloride in concentrated hydrochloric acid. Distillation with steam at 140° then removed 3 : 5-dinitrochlorobenzene; the residue in the flask gave, after recrystallisation, a 15—20% yield of 3 : 3′ : 5 : 5′-tetranitrodiphenyl. The dinitrochlorobenzene was reduced with ammonium sulphide, and the 5-chloro-*m*-nitroaniline obtained was converted into 3 : 5-dichloronitrobenzene in the usual way. Reduction in alcoholic solution with iron dust and a trace of hydrochloric acid then gave an 80% yield of 3 : 5-dichloroaniline in slender needles, m. p. 50° (Witt, *Ber.*, 1875, **8**, 145; Beilstein and Kurbatow, *Annalen*, 1875, **176**, 219).

3 : 4 : 5-*Trichloroaniline*.—2 : 6-Dichloro-4-nitroaniline (prepared by the action of potassium chlorate on a solution of *p*-nitroaniline in dilute hydrochloric acid) (1 mol.) was dissolved in acetic acid (10 vols.) and concentrated sulphuric acid (2 mols.), cooled to 0°,

and treated with methyl nitrite. The diazotised solution was heated with a solution of cuprous chloride in concentrated hydrochloric acid, and the trichloronitrobenzene isolated by steam distillation. Reduction with tin and hydrochloric acid then gave 3 : 4 : 5-trichloroaniline in white needles, m. p. 89°.

3 : 4 : 6-*Trichloroaniline.*—The methods of Lesimple (*Annalen*, 1866, **137**, 125), Beilstein and Kurbatow (*ibid.*, 1879, **196**, 232), and Gleube and Rostowzein (*Ber.*, 1901, **34**, 211) having proved inconvenient, this compound was prepared by chlorinating *m*-chloroacetanilide until the increase in weight corresponded with the introduction of two molecules of chlorine; on hydrolysis the trichloroaniline was obtained in small crystals, m. p. 95°.

2 : 3 : 5 : 6-*Tetrachloroaniline.*—The methods of Beilstein and Kurbatow (*Annalen*, 1879, **196**, 236) and Hentschel (*Ber.*, 1898, **31**, 248) are unsatisfactory.

A solution of 50 g. of 1 : 2 : 4 : 5-tetrachlorobenzene in warm fuming nitric acid (150 c.c.) was poured into water and the orange product, which contained tetrachlorobenzoquinone, was collected and extracted three times with boiling light petroleum. The extracts were evaporated on a steam-bath; on recrystallising the residue from alcohol, tetrachloronitrobenzene was obtained in pale yellow needles, m. p. 99°. Reduction with tin and hydrochloric acid gave 12 g. of 2 : 3 : 5 : 6-tetrachloroaniline, m. p. 90°.

The authors desire to express their gratitude to the Research Fund Committee of the Chemical Society and to the Trustees of the Dixon Fund of the University of London for grants which have helped to defray the cost of the materials used in this investigation.

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[*Received, September 4th*, 1926.]

CCCCVII.—*Investigations in the Diphenyl Series. Part III. Derivatives of* 4-*Hydroxydiphenyl.*

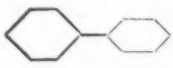
By FRANK BELL and JOSEPH KENYON.

IT has been suggested (Turner, *Nature*, 1923, **112**, 439) that the asymmetry of the diphenyl derivatives resolved by Kenner (J., 1922, **121**, 614, *et seq.*) is due to the presence of a permanent bond between the 4- and the 4′-position (I). Abnormal reactivity of the hydrogen atom in the 4′-position subsequent to the introduction of

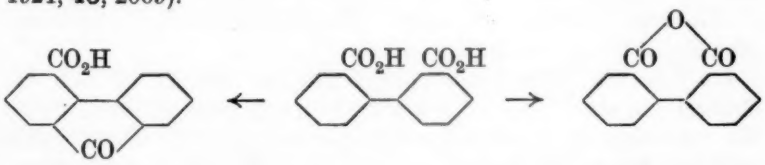
a suitable group in the 4-position would be strongly indicative of such a direct connexion. It is well known that the *p*-hydrogen atom of both dimethylaniline and phenol is specially reactive, but no such reactivity has been found in the corresponding diphenyl derivatives: 4-dimethylaminodiphenyl neither condenses with benzaldehyde nor couples with diazotised aniline or diazotised sulphanilic acid, whilst with nitrous acid it yields 3-nitro-4-dimethylaminodiphenyl (Garciá Banús and Ferrer Tomás, *Anal. Fis. Quím.*, 1921, **19**, 293; Vorländer, *Ber.*, 1925, **58**, 1913).

4-Hydroxydiphenyl couples readily with diazotised aniline; the coupling, however, occurs in the 3-position. Similarly, with nitrous acid the product is 3-nitro-4-hydroxydiphenyl. A structure of type (I) would demand that, in the Reimer-Tiemann reaction, 4-hydroxydiphenyl should give 4-hydroxy-4′-aldehydodiphenyl: although no conclusive proof has been obtained, there is little doubt that the product is 4-hydroxy-3-aldehydodiphenyl.

The experimental results at present available suggest that (1) free rotation of the two nuclei is possible in all lightly-substituted diphenyl derivatives; (2) when free rotation is inhibited, the two nuclei adopt configuration (II), in which they have a common axis but are no longer co-planar.

(I.)  (II.)

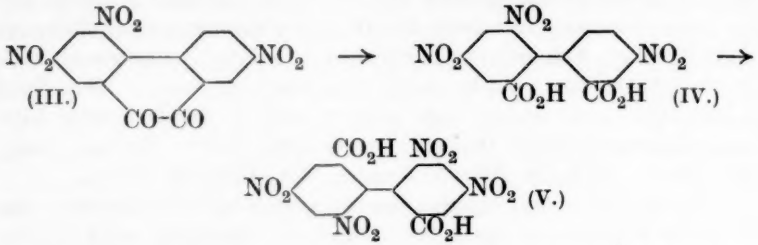
Hypothesis (1) is in harmony with the facts that attempts to resolve diphenic acid and methyl hydrogen diphenate have been unsuccessful * and that diphenic acid and its derivatives readily yield anhydrides on the one hand and fluorenonecarboxylic acids on the other (Underwood and Kochmann, *J. Amer. Chem. Soc.* 1924, **46**, 2069).



Hypothesis (2) appears to be more in harmony with the experimental facts than the Kaufler configuration, since no evidence exists that the 4 : 4′-positions are close to each other (compare Le Fèvre and Turner, this vol., p. 2476). Moreover, it obviates the necessity for assuming frequent changes of configuration such as

* This is in marked contrast with the behaviour of 6-nitrodiphenic acid, which is readily resolvable.

the following, where the method of preparation of (IV) suggests a *cis*-structure, whereas the resolution of (V) requires a *trans*-structure.



4-Methoxydiphenyl on nitration yields a mixture of 3-nitro-4-methoxydiphenyl (about 80%) and 4′-nitro-4-methoxydiphenyl (about 15%); that these derivatives possess the above constitutions was established by preparing them from the corresponding nitrophenols. 4′-Nitro-4-hydroxydiphenyl was described by Schmidt and Schultz (*Annalen*, 1881, **207**, 347), but from the experiments herein described it would appear that the compound obtained by them was, in all probability, 3 : 4′-dinitro-4-hydroxydiphenyl. 4′-Nitro-4-methoxydiphenyl very readily nitrates to give 3 : 4′-dinitro-4-methoxydiphenyl, which was also obtained in 50% yield by the nitration of 3-nitro-4-methoxydiphenyl.

Raiford and Colbert (*J. Amer. Chem. Soc.*, 1925, **47**, 1456) have described the dibromination of 4-hydroxydiphenyl and the nitration of the resulting dibromohydroxydiphenyl to give a dibromomononitro-4-hydroxydiphenyl, m. p. 171°. A dibromo-4′-nitro-4-hydroxydiphenyl, m. p. 232—234°, has now been prepared by the bromination of 4′-nitro-4-hydroxydiphenyl and it can scarcely be other than 3 : 5-dibromo-4′-nitro-4-hydroxydiphenyl. It appears, therefore, that the dibromophenol cannot be, as Raiford and Colbert suggested, 3 : 5-dibromo-4-hydroxydiphenyl. The halogenation of 4-hydroxydiphenyl is being examined in detail.

4-*p*-Toluenesulphonyloxydiphenyl nitrates mainly, if not exclusively, in the 4′-position, a result which is in marked contrast with the nitration of 4-*p*-toluenesulphonaminodiphenyl, which yields only the 3-nitro-derivative (compare Part II, this vol., p. 2708). It is suggested that the difference in behaviour may be due to substitution being possible *via* the directing group in the former case, whereas in the latter direct substitution only can take place.

Experimental.

4-Hydroxydiphenyl, prepared in 60% yield by the diazotisation of 4-aminodiphenyl, is readily purified by crystallisation from

benzene. It does not form an additive compound when warmed with *p*-benzoquinone in benzene solution.

Reaction with Nitrous Acid.—Sodium nitrite (1 mol.), followed by hydrogen peroxide, was added to a solution of 4-hydroxydiphenyl in warm acetic acid. The mixture was gently heated for a short time and poured into water and the precipitate of 3-nitro-4-hydroxydiphenyl was crystallised from methyl alcohol.

2-*Hydroxy*-5-*phenylazobenzene.*—Diazotised aniline (1 mol.) was added to a cooled solution of 4-hydroxydiphenyl in dilute aqueous sodium hydroxide. The reddish-brown deposit that formed immediately was filtered off, washed with water, and recrystallised from alcohol, being obtained as brick-red needles, m. p. 129° (Found : C, 78·45; H, 5·2. $C_{18}H_{14}ON_2$ requires C, 78·8; H, 5·1%).

This compound was reduced by sodium hyposulphite to 3-amino-4-hydroxydiphenyl, m. p. 208° after crystallisation from chloroform. This value agrees with that given by Raiford and so also does that for the diacetyl derivative.

4-*Hydroxy*-3(?)-*aldehydodiphenyl.*—4-Hydroxydiphenyl (16 g.) was heated under reflux for 3 hours with a mixture of chloroform (20 g.), sodium hydroxide (20 g.), and water (500 c.c.) and the solution was filtered hot. The residue was dissolved in boiling water, and the filtered solution decomposed with hydrochloric acid. The precipitated aldehyde crystallised from alcohol in pale yellow plates, m. p. 102° (Found : C, 79·0; H, 5·3. $C_{13}H_{10}O_2$ requires C, 78·8; H, 5·1%), which gave an intense violet coloration with ferric chloride. The *phenylhydrazone*, precipitated on addition of phenylhydrazine to a warm alcoholic solution of the aldehyde, crystallised from benzene in needles, m. p. 210° (Found : C, 79·5; H, 5·9. $C_{19}H_{16}ON_2$ requires C, 79·2; H, 5·5%).

Attempted Resolution of Diphenic Acid.— The brucine and quinine salts of diphenic acid were crystallised from various solvents without any sign of resolution being observed. The α-phenylethylamine salt was obtained as a viscous oil. The strychnine, morphine, and brucine salts of methyl hydrogen diphenate were crystallised from various solvents, but no resolution could be detected. The quinine salt was obtained as a gum.

Nitration of 4-*Methoxydiphenyl.*—To a solution of 4-methoxydiphenyl (7·4 g.) in acetic anhydride (40 c.c.) was added nitric acid (*d* 1·5; 2 c.c.) in acetic anhydride (8 c.c.). Reaction took place with evolution of heat, and after 1 hour the mixture was poured into water. Repeated crystallisation of the precipitated nitro-compounds from alcohol gave 4·2 g. (45%) of 3-*nitro*-4-*methoxydiphenyl.* On evaporation of the mother-liquor 5 g. of material, m. p. 50—75°, were obtained. This could not be purified

by further crystallisation and therefore was renitrated in a mixture of nitric acid (*d* 1·42; 10 c.c.) and acetic acid (10 c.c.). When reaction was complete the mixture was poured into water, and the precipitate, m. p. 125—135°, boiled with alcohol (200 c.c.). The residue, after repeated crystallisation from benzene, acetic acid, or chloroform, melted at 163—166°, but analysis showed that it was contaminated with mononitro-derivatives. It was therefore warmed for a few minutes with nitric acid; an apparently uniform product, m. p. 171°, was then obtained. No other compound could be isolated from the more soluble material (2·5 g., m. p. 125—150°). Addition of nitric acid (1 mol.) to a solution of 4′-nitro-4-methoxydiphenyl in acetic anhydride gave a quantitative yield of the product, m. p. 171°, which was also obtained in 50% yield by treating 3-nitro-4-methoxydiphenyl with warm nitric acid (*d* 1·42), its identity as 3 : 4′-*dinitro*-4-*methoxydiphenyl* thus being established (Found : C, 56·4; H, 3·6. $C_{13}H_{10}O_5N_2$ requires C, 56·9; H, 3·7%).

Since, under the conditions of the nitration of the product, m. p. 50—75°, 3-nitro-4-methoxydiphenyl suffers only 25% conversion into 3 : 4′-dinitro-4-methoxydiphenyl, it is apparent that the mixture, m. p. 50—75°, must contain about 25% of 4′-nitro-4-methoxydiphenyl. The results indicate that 4-methoxydiphenyl on nitration gives approximately 80% of 3-nitro-4-methoxydiphenyl and 15% of 4′-nitro-4-methoxydiphenyl.

3-*Nitro*-4-*methoxydiphenyl*, obtained by boiling a solution of 3-nitro-4-hydroxydiphenyl in xylene with potassium carbonate and methyl sulphate, crystallised from alcohol in small needles, m. p. 91—92° (Found : C, 68·3; H, 4·7. $C_{13}H_{11}O_3N$ requires C, 68·1; H, 4·8%).

4′-*Nitro*-4-*methoxydiphenyl*.—Small quantities of methyl sulphate and potassium hydroxide were added to a hot solution of 4′-nitro-4-hydroxydiphenyl in dilute aqueous potassium hydroxide until the red colour disappeared; the suspension was filtered hot. The precipitated 4′-*nitro*-4-*methoxydiphenyl* crystallised from alcohol in long, yellow needles, m. p. 111° (Found : C, 68·5; H, 4·9. $C_{13}H_{11}O_3N$ requires C, 68·1; H, 4·8%).

3 : 5-*Dinitro*-4-*methoxydiphenyl*, obtained by boiling a solution of 3 : 5-dinitro-4-hydroxydiphenyl in xylene with potassium carbonate and methyl sulphate, crystallised from alcohol in silky, yellow needles, m. p. 137—138° (Found : C, 56·8; H, 3·7. $C_{13}H_{10}O_5N_2$ requires C, 56·9; H, 3·7%).

4′-*Nitro*-4-*hydroxydiphenyl*.—4′-Nitro-4-aminodiphenyl (6 g.) was dissolved in boiling dilute hydrochloric acid (500 c.c. of 1%), the clear solution rapidly cooled to 10°, and sodium nitrite (2·4 g.) added. After standing for 1 hour with occasional shaking, the

solution was filtered, dilute sulphuric acid added, and the bulky precipitate of the diazonium sulphate decomposed by passing in steam. The precipitate thus obtained was filtered off and extracted with boiling dilute aqueous potassium hydroxide. The extract was acidified with hydrochloric acid and the crude nitrophenol thus precipitated was filtered off and boiled with alcohol (100 c.c., which leaves any dinitrophenol undissolved), and the filtered alcoholic extract was evaporated to dryness. The residue was crystallised from benzene; *4′-nitro-4-hydroxydiphenyl* was then obtained in lustrous, yellow needles, m. p. 203° (yield, 60%) (Found: C, 67·3; H, 4·4. $C_{12}H_9O_3N$ requires C, 67·0; H, 4·2%).

3 : 4′-*Dinitro-4-hydroxydiphenyl*, prepared by adding a slight excess of sodium nitrite to a solution of 4′-nitro-4-hydroxydiphenyl in warm acetic acid, crystallised from acetic acid in small needles, m. p. 172° (Found: C, 55·6; H, 3·1. $C_{12}H_8O_5N_2$ requires C, 55·4; H, 3·1%). Further nitration gave 3 : 5 : 4′-trinitro-4-hydroxydiphenyl. The dinitro-compound reacted with *p*-toluenesulphonyl chloride in pyridine solution and gave a p-*toluenesulphonate* which crystallised from benzene–light petroleum in star-shaped clusters of needles, m. p. 147—148° (Found: C, 54·7; H, 3·5; N, 6·5. $C_{19}H_{14}O_7N_2S$ requires C, 55·1; H, 3·4; N, 6·75%).

(3 : 5 ?)-*Dibromo-4′-nitro-4-hydroxydiphenyl*.—4′-Nitro-4-hydroxydiphenyl (1 g.) was heated under reflux with a solution of bromine (2 g.) in chloroform (20 c.c.). The crystals which gradually formed were filtered off and when recrystallised from benzene gave small needles, m. p. 232—234° (Found: C, 39·0; H, 1·9. $C_{12}H_7O_3NBr_2$ requires C, 38·6; H, 1·9%).

4-p-*Toluenesulphonyloxydiphenyl*, prepared by the interaction of 4-hydroxydiphenyl and *p*-toluenesulphonyl chloride in pyridine solution, crystallised from acetic acid in lustrous plates, m. p. 177° (Found: C, 70·5; H, 5·2. $C_{19}H_{16}O_3S$ requires C, 70·4; H, 4·9%).

4-p-*Toluenesulphonyloxy-4′-nitrodiphenyl*.—(*a*) 2·5 G. of the preceding compound were added to a warmed mixture of nitric acid (*d* 1·5; 2·5 c.c.) and acetic acid (3 c.c.) and after ½ hour the clear solution was poured on to ice. The precipitated plastic mass was extracted with a little hot alcohol to remove impurities. The residue crystallised from benzene–light petroleum in compact needles, m. p. 156—158° (Found: C, 62·3; H, 4·3. $C_{19}H_{15}O_5NS$ requires C, 61·8; H, 4·1%).

(*b*) 4′-Nitro-4-hydroxydiphenyl (1 g.) was warmed for 4 hours with a solution of *p*-toluenesulphonyl chloride (1 g.) in diethylaniline (5 c.c.). The solution was digested with hydrochloric acid and filtered; the residue, after crystallisation from benzene, melted at 159°.

One of the authors (F. B.) is in receipt of a grant from the Advisory Council of the Department of Scientific and Industrial Research, for which he wishes to express his indebtedness.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, September 24th*, 1926.]

CCCCVIII.—*Investigations in the Diphenyl Series. Part IV. Halogenation of 4-Aminodiphenyl.*

By JOSEPH KENYON and PERCY HARRY ROBINSON.

THE divergence in the action of chlorine and of bromine on 4-acetylaminodiphenyl in acetic acid solution was briefly recorded in Part I (this vol., p. 1242). Bromine, unlike chlorine, gives rise to two isomerides, *viz.*, 3- and 4′-bromo-4-acetylaminodiphenyl, which comprise about 50% and 30% of the product, respectively; small quantities of the corresponding bromo-bases are sometimes produced by hydrolysis. The orientation of the two principal products has been determined as follows : 4′-bromo-4-aminodiphenyl obtained by hydrolysis of its acetyl derivative is identical with 4′-bromo-4-aminodiphenyl prepared from benzidine by the usual method; the 3-bromo-4-aminodiphenyl similarly obtained was converted into 3 : 5-dibromo-4-aminodiphenyl, which has been described by Scarborough and Waters (this vol., p. 557).

The results of the bromination of 4-acetylaminodiphenyl herein described differ considerably from those recorded by those authors, who did not observe the formation of 3-bromo-4-acetylaminodiphenyl.

3-Bromo-4-aminodiphenyl was the only product isolated from the interaction of *N*-bromoacetanilide and 4-aminodiphenyl.

3 : 5-Dibromo-4-aminodiphenyl is converted with great readiness into a monoacetyl and a diacetyl derivative, which melt respectively at 212° and 184°; it seems likely, therefore, that the acetyl derivative of 3 : 5-dibromo-4-aminodiphenyl, m. p. 162°, described by Scarborough and Waters is a mixture. It is somewhat remarkable that this base should undergo di-acetylation with great readiness, a property which is shared by (3 : 5 ?)-dibromo-4′-nitro-4-aminodiphenyl.

A striking difference in stability is shown by the *N*-halogeno-derivatives of 4-acetylaminodiphenyl, for whilst *N*-chloro-4-acetylaminodiphenyl and 4′ : *N*-dichloro-4-acetylaminodiphenyl can be obtained pure and exhibit the normal degree of stability, 3 : *N*-dichloro-4-acetylaminodiphenyl and *N*-bromo-4-acetylaminodiphenyl lose halogen with great readiness and cannot be obtained pure.

The failure to obtain the latter compound is unfortunate, as it was hoped that its behaviour on treatment with acetic acid might explain the divergence in the action of bromine and of chlorine on 4-acetylaminodiphenyl referred to above. 4′ : *N*-Dichloro-4-acetylaminodiphenyl in acetic acid solution undergoes transformation to 3 : 4′-dichloro-4-acetylaminodiphenyl, which was also isolated in small quantity (5%) from the products of the action of hot acetic acid on the unstable 3 : *N*-dichloro-4-acetylaminodiphenyl.

This result may be compared with the behaviour of *oN*-dichloroacetanilide, which does not undergo complete conversion into 2 : 4-dichloroacetanilide even when heated in acetic acid solution at 100° for many hours (Chattaway and Orton, J., 1900, **77**, 797).

3 : 4′-Dichloro-4-acetylaminodiphenyl was identified by conversion into 3 : 5 : 4′-trichloro-4-acetylaminodiphenyl, a compound which has been described by Scarborough and Waters (*loc. cit.*).

Only one product could be isolated from the bromination of 4-dimethylaminodiphenyl, and from its great solubility and low m. p. it is presumed to be 3-bromo-4-dimethylaminodiphenyl.

In the case of diphenyl derivatives with an ortho-para-directing group in position 4, it would therefore seem possible to draw the following conclusions: (1) Whilst migration substitution can occur only in the 3-position, direct substitution can take place in positions 3 and 4′. (2) When a second ortho-para-directing substituent of almost equal power is present in position 3, substitution occurs in the 4′-position and migration substitution is inhibited.

Experimental.

3-Bromo-4-acetylaminodiphenyl.—Bromine (27·8 g.) dissolved in glacial acetic acid (30 c.c.) was added to a solution of 4-acetylaminodiphenyl (35 g.) in glacial acetic acid (400 c.c.), and the mixture maintained at 30—40° for an hour. The crystalline precipitate that separated (27 g.) was collected after some time, ground with dilute sodium carbonate solution, washed, dried, and well shaken with cold benzene (100 c.c.), in which 4′-bromo-4-acetylaminodiphenyl is only sparingly soluble. The filtered extract was evaporated to dryness and the residue recrystallised from alcohol; after removal of a further quantity of the less soluble 4′-bromo-isomeride, impure 3-bromo-4-acetylaminodiphenyl was obtained. The greater portion of this compound, however, remained in the acetic acid solution, from which it was obtained (29·5 g.) by precipitation with water. Extraction of this material, when dry, with cold benzene removed much of the 4′-bromo-isomeride present (more than 5%), but even fractional crystallisation from alcohol usually failed to raise the m. p. above 146°, since this procedure did not completely remove

the admixed 4′-bromo-4-acetylaminodiphenyl, unchanged 4-acetylaminodiphenyl and some dibrominated material. Complete purification of the material of m. p. 146° was effected most conveniently by hydrolysis: the resulting crude 3-bromo-4-aminodiphenyl, after crystallisation and reacetylation, gave the pure *acetyl* derivative, which separated from alcohol or light petroleum in long, glistening needles, m. p. 161° (Found: Br, 27·9. $C_{14}H_{12}ONBr$ requires Br, 27·6%).

3-*Bromo*-4-*aminodiphenyl*, obtained from its acetyl derivative by hydrolysis with alcoholic hydrogen chloride or 65% sulphuric acid, crystallised from aqueous alcohol in almost colourless, small plates, m. p. 66° (Found: C, 57·8; H, 4·0. $C_{12}H_{10}NBr$ requires C, 58·0; H, 4·0%). When mixed with cold acetic anhydride, this substance dissolved at once, and almost immediately separated in the form of its acetyl derivative. To a solution of the free base in cold acetic acid, bromine (1 mol.) was added; the yellow precipitate which formed was washed with sodium carbonate solution and dissolved in alcohol, from which it separated in needles, m. p. 118°, identical with the 3:5-dibromo-4-aminodiphenyl obtained by the direct bromination of 4-aminodiphenyl.

4′-Bromo-4-acetylaminodiphenyl requires heating with 75% sulphuric acid at 120—130° for some hours before hydrolysis is complete.

3:5-*Dibromo*-4-*acetylaminodiphenyl* was obtained by heating a mixture of 3:5-dibromo-4-aminodiphenyl (24 g.), acetic acid (120 c.c.), and acetic anhydride (14 c.c.) under reflux for 2 hours and pouring the reaction mixture into water. The dried precipitate was extracted with carbon tetrachloride (250 c.c.), and the residue (22 g.) crystallised from alcohol, from which it separated in long needles, m. p. 212° (Found: C, 45·5; H, 3·2. $C_{14}H_{11}ONBr_2$ requires C, 45·5; H, 3·0%).

3:5-*Dibromo*-4-*diacetylaminodiphenyl*, obtained by the process described above when a higher concentration of acetic anhydride was used, crystallised from carbon tetrachloride in short needles, m. p. 184° (Found: C, 46·8; H, 3·1. $C_{16}H_{13}O_2NBr_2$ requires C, 46·7; H, 3·2%).

(3?)-*Bromo*-4-*dimethylaminodiphenyl*.—To 4-dimethylaminodiphenyl (8 g.) dissolved in acetic acid, bromine (6·5 g.), diluted with acetic acid, was added and after ¼ hour the reaction mixture was poured into water and neutralised with ammonia. The precipitate was dissolved in dilute hydrochloric acid, reprecipitated with ammonia, and crystallised from methyl alcohol, forming lustrous plates, m. p. 82° (Found: C, 60·9; H, 5·2. $C_{14}H_{14}NBr$ requires C, 60·8; H, 5·1%).

(3 : 5 ?)-*Dibromo*-4′-*nitro*-4-*acetylaminodiphenyl*.—4′-Nitro-4-aminodiphenyl (3·5 g.) (obtained in 70—75% yield by the method of Willstätter, *Ber.*, 1906, **39**, 3478) was warmed with bromine (5·5 g.) and acetic acid (30 c.c.) for several hours, and the mixture poured into water. After several recrystallisations from benzene the product formed pale yellow needles, m. p. 184° (Found : C, 40·3; H, 2·5. $C_{14}H_{10}O_3N_2Br_2$ requires C, 40·6; H 2·4%). On boiling with acetic anhydride for 1 hour, this compound was converted into (3 : 5 ?)-*dibromo*-4′-*nitro*-4-*diacetylaminodiphenyl*, which crystallised from acetic acid in needles, m. p. 228° (Found : C, 42·1; H, 2·7. $C_{16}H_{12}O_4N_2Br_2$ requires C, 42·1; H, 2·6%). The positions assigned to the bromine atoms could not be confirmed, as 3 : 5-dibromo-4-acetylaminodiphenyl, under conditions sufficiently powerful to cause nitration, gave a product from which only a dinitro-derivative could be obtained in a pure state.

3 : 5-*Dibromodinitro*-4-*acetylaminodiphenyl* crystallised from acetic acid in clusters of small needles, m. p. 269—270° (Found : C, 36·9; H, 2·4. $C_{14}H_9O_5N_3Br_2$ requires C, 36·6; H, 2·0%). By boiling for 1 hour with acetic anhydride it was converted into 3 : 5-*dibromodinitro*-4-*diacetylaminodiphenyl*, which crystallised from aqueous acetic acid in stout needles, m. p. 140° (Found : C, 38·8; H, 2·3. $C_{16}H_{11}O_6N_3Br_2$ requires C, 38·4; H, 2·2%).

Action of N-*Bromoacetanilide on* 4-*Aminodiphenyl*.—*N*-Bromoacetanilide (5·3 g.; Chattaway and Orton, J., 1899, **75**, 1046) was dissolved in chloroform and added slowly to a chloroform solution of 4-aminodiphenyl (4 g.); a deep red colour developed. The residue obtained from the solution after evaporation was hydrolysed with alcoholic hydrogen chloride, and the freed aniline removed by steam-distillation. Recrystallisation of the product yielded only 3-bromo-4-aminodiphenyl.

4′ : N-*Dichloro*-4-*acetylaminodiphenyl*.—Finely-divided 4′-chloro-4-acetylaminodiphenyl (6·9 g.), obtained by pouring an alcoholic solution into water, was suspended in water (300 c.c.) containing potassium bicarbonate (7 g.) and mixed with sodium hypochlorite (excess of *N*/4-solution) and the whole was maintained at 60° for an hour. The product separated from carbon tetrachloride or from chloroform–light petroleum in almost colourless, small plates; m. p. 128°. The compound solidified just above its m. p. and then melted at 181° (Found : Cl, 12·4, by estimation of the iodine liberated from potassium iodide. $C_{14}H_{11}ONCl_2$ requires Cl, 12·7%).

3 : 4′-*Dichloro*-4-*acetylaminodiphenyl* was easily prepared by dissolving the chloroamine in warm acetic acid; it separated on cooling and crystallised from carbon tetrachloride in large, colour

less needles, m. p. 184° (Found : C, 59·9; H, 3·9. $C_{14}H_{11}ONCl_2$ requires C, 60·0; H, 3·9%). It was also obtained in small quantity from 3-chloro-4-acetylaminodiphenyl, which, with hypochlorous acid, gave an unstable chloroamine. This substance, on solution in acetic acid, gave as the principal product of the reaction 3-chloro-4-acetylaminodiphenyl accompanied by less than 5% of 3 : 4′-dichloro-4-acetylaminodiphenyl.

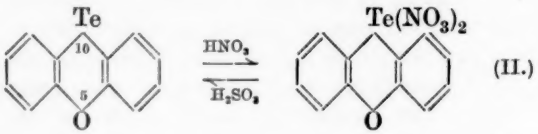
When an acetic acid solution of the latter compound was mixed with an excess of sodium hypochlorite solution, 3 : 5 : 4′-trichloro-4-acetylaminodiphenyl (compare Scarborough and Waters, *loc. cit.*) was obtained, the view that the dichloro-4-acetylaminodiphenyl is the 3 : 4′-isomeride thus being confirmed.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, October 13th*, 1926.]

CCCCIX.—*Cyclic Organo-metallic Compounds. Part II. Tellurylium Compounds, a New Series of Intensely Coloured Tellurium Derivatives. The Migration of Anions in Solids.*

By HARRY DUGALD KEITH DREW.

WHEN phenoxtellurine (I) is treated with nitric acid under conditions which preclude nitration of the nucleus, it becomes intensely bluish-violet and is then transformed to colourless phenoxtellurine dinitrate (II; see this vol., p. 223). Reduction of the dinitrate with sulphurous acid gives a similar bluish-violet, intermediate substance, which is ultimately transformed completely to yellow phenoxtellurine. Each of the following processes, therefore, gives rise to an intensely coloured compound :

(I.) 

(II.)

An insight was obtained into the nature of the phenomenon when it was found that the intense violet colour was developed on merely mixing and rubbing together the dry substances (I and II) between glass surfaces. The action of such solvents as water, alcohol, ether, benzene, and chloroform discharged the colour, reproducing the original substances, which could be recovered and

recombined. A glass rod coated with a film of the violet substance became colourless on being plunged into ether vapour, the colour returning on withdrawal into the air.

A series of nitro- and dinitro-derivatives of substance (II), of which 2-*nitrophenoxtellurine* 10 : 10-*dinitrate* and 2 : 8-*dinitrophenoxtellurine* 10 : 10-*dinitrate* are examples, was next prepared; and it was found that these substances produced similar violet compounds when combined with phenoxtellurine or with a nitro- or dinitro-derivative thereof, although, owing to steric or other hindrance, not every pair could be caused to interact (see table, p. 3066).

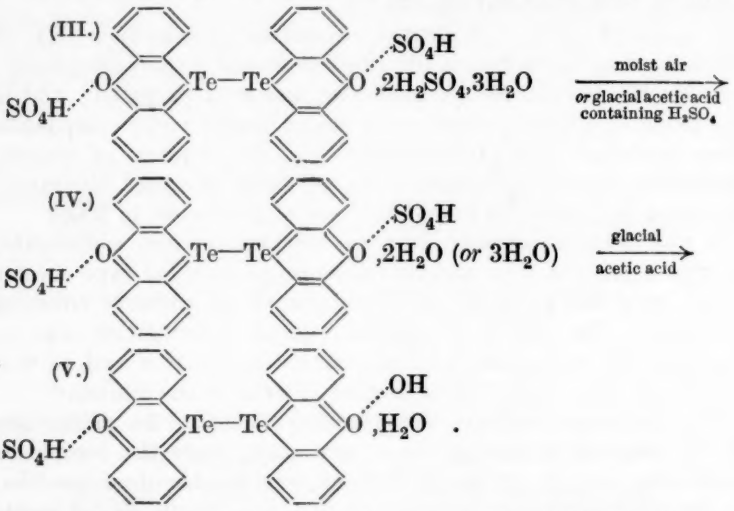
It was therefore evident that the reaction between a dinitrate, of type similar to (II), and its reduction product, of type similar to (I), occasions generally the formation of an intensely coloured substance. The object of the subsequent investigation was to elucidate the mechanism of this remarkable reaction and to find the extent of its applicability to salts other than the dinitrates.

The foregoing methods were inconvenient for the production of the coloured substances in a pure state, since the complexes containing nitrate groups underwent considerable decomposition in the most favourable solvent medium, *viz.*, warm glacial acetic acid. The possibility of substituting the less oxidising bisulphate radical for the nitrate radical was therefore examined.

The author had previously noted (*loc. cit.*) the production of an intensely red colour when phenoxtellurine was dissolved in concentrated sulphuric acid. This reaction is accompanied by the evolution of sulphur dioxide, pointing to the intermediate production of a sulphate of phenoxtellurine. To isolate the colouring matter, water was cautiously mixed in small proportion with the red solution, and the liquid allowed to stand. There separated bright red crystals of *diphenoxtellurylium dibisulphate disulphuric acid trihydrate* (III). On exposure on porous tile to moist air, this hygroscopic substance loses the attached "free" sulphuric acid, and becomes transformed quantitatively into an intensely violet-blue substance having a greenish-bronze reflex, *viz.*, *diphenoxtellurylium dibisulphate di-* or *tri-hydrate* (IV), in which the conditions of drying determine the final degree of hydration.

Similarly, when the red solution of phenoxtellurine in concentrated sulphuric acid was diluted with a greater proportion of water, the colour changed from red to blue with eventual production of a violet precipitate; and the latter, when crystallised from glacial acetic acid, was transformed into *diphenoxtellurylium hydroxybisulphate monohydrate* (V), which separated in copper-coloured needles giving a violet-black powder. The change was evidently

due to the removal of part of the water followed by hydroxylation of one of the bisulphate radicals of the intermediate compound (IV).



(The dotted bonds in the above and the following formulæ indicate polar linkings.)

Crystallisation of the red compound (III) from glacial acetic acid likewise resulted in the almost quantitative production of compound (V), "free" sulphuric acid and water being removed, part of the latter then producing hydroxylation. When, however, compound (III) was dissolved in acetic anhydride, which would have the effect of permanently removing the water, it was decomposed without production of (V), behaviour which confirms the foregoing view of the change in glacial acetic acid.

The above changes and the additional reactions indicated in the following statement show that the transformation of the three compounds (III, IV, and V) can be carried out in either direction:

(i) Crystallisation of (III) from glacial acetic acid containing a little conc. H_2SO_4 yields (IV).
(ii) Crystallisation of (V) from glacial acetic acid containing considerable conc. H_2SO_4 yields (III).
(iii) The action of (I) on glacial acetic acid containing a little conc. H_2SO_4 yields (IV), together with SO_2.
(iv) The action of (I) on glacial acetic acid containing more conc. H_2SO_4 yields (III), together with SO_2.

Each of the compounds (III), (IV), and (V) is decomposed into its constituents by an excess of water. The reaction is quantitative in a rough sense; and it has been shown that approximately equimolecular proportions of phenoxtellurine and its (hydroxylated

salt are produced in each case, these substances being readily separable. It thus becomes clear why the gradual addition of water to a solution of phenoxtellurine in concentrated sulphuric acid changes the red colour to blue and violet and finally leaves only a pale yellow turbidity due to phenoxtellurine.

Each of the nitro- and dinitro-substituted phenoxtellurines yields an intensely coloured violet or greenish-violet substance when its red solution in sulphuric acid is cautiously diluted with water. The same holds even in the case of 2 : 8-diaminophenoxtellurine.

Compound (V) shows remarkable behaviour in glacial acetic acid solution. It is practically insoluble in the cold; but in the hot solvent it gives intense cherry-red solutions which become very pale yellow when diluted with more solvent. Solutions sufficiently dilute to be nearly colourless when hot develop intense cherry-red colorations on cooling, whilst more concentrated solutions become cherry-red and then deep violet-blue on cooling, owing to the deposition of the finely-divided solid. Compound (IV) shows similar behaviour.

It will be clear that, on the foregoing hypothesis, the violet compounds (IV and V) result from a combination of phenoxtellurine and its dibisulphate or hydroxybisulphate. To confirm this view, it was necessary to combine these constituents directly.

To obtain the sulphate, it was found best to prepare first *phenoxtellurine* 10 : 10-*diacetate*, $O<^{C_6H_4}_{C_6H_4}>Te(O\cdot CO\cdot CH_3)_2$ (VI). This was readily obtained, in the form of colourless needles soluble in organic solvents, by the action (i) of hydrogen peroxide, or (ii) of sodium nitrite, upon a glacial acetic acid solution of phenoxtellurine; and these reactions were found to be of general application to the members of the phenoxtellurine and *cyclo*telluropentanedione series of tellurides.

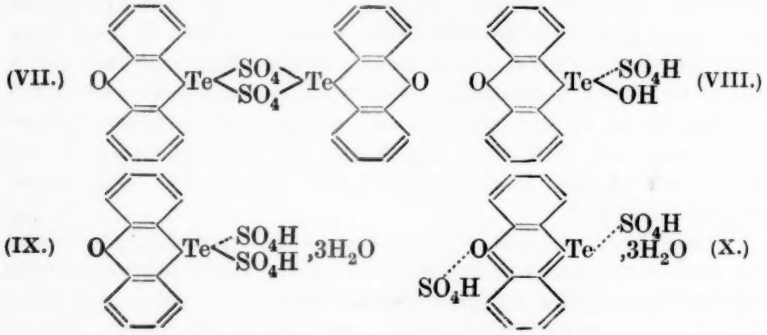
The use of an excess of hydrogen peroxide occasions the production of *phenoxtellurone*, an insoluble white powder (see experimental section).

When a solution of phenoxtellurine diacetate (VI) in boiling water was treated with sulphuric acid, a crystalline sulphate separated, which, on recrystallisation from sulphuric acid, gave crystals whose composition depended upon the concentration of acid present. With the minimum of sulphuric acid necessary to cause precipitation, almost colourless needles of *phenoxtellurine sulphate* (VII; or, less probably, its monomeric form) separated. This substance occasioned little, if any, development of colour with phenoxtellurine.

From more strongly acid solutions, cream-coloured crystals were

obtained, approximating in composition to a complex compound (see experimental section) containing phenoxtellurine hydroxybisulphate (VIII). This substance (or mixture) gave considerable development of violet colour when rubbed with phenoxtellurine.

When, however, the crude sulphate was dissolved in warm concentrated sulphuric acid, and a relatively small proportion of water added, the orange solution crystallised on cooling to a mass of yellow plates, which, after being drained on clay in a desiccator, became transformed into pale yellow *phenoxtellurine dibisulphate trihydrate* (IX), obtained in a pure state.



This substance combined with tellurides to form intensely violet products. With phenoxtellurine, either in the dry state or in presence of glacial acetic acid, compound (IV) was produced; and, from it, compounds identical with (III) and (V) were readily obtained in the pure condition.

These syntheses demonstrate the truth of the initial hypothesis.

Phenoxtellurine dibisulphate, unlike the dinitrate and diacetate, is yellow. Its solution in sulphuric acid is bright yellow, or orange-red when hot or concentrated. For this reason, formula (X) must be considered as an alternative to formula (IX), or, at least, as representing a possible phase. In any case, phenoxtellurine dibisulphate behaves as a salt, and must be considered to possess one anion in the phase represented by (IX), and possibly two anions in that represented by (X).

When phenoxtellurine diacetate is treated with syrupy phosphoric acid or with a concentrated solution of perchloric acid, salts are obtained which resemble the dinitrate and dibisulphate in that they give rise to intensely coloured tellurylium compounds (although of a bluer shade) when combined with tellurides. The salts are probably di-dihydrogen phosphates and diperchlorates, respectively. They and the derived tellurylium compounds are extremely sensitive to moisture.

Telluride salts containing nitrate, bisulphate, dihydrogen phosphate, or perchlorate radicals therefore possess an anion, and, when this migrates from tellurium (as in X), a further anion may develop. The tellurium atom in these cases is satisfied with one polar and three non-polar bonds; but where chloride, bromide, or acetate radicals are present, the compounds are non-polar and do not give rise to coloured complexes. The tellurium atom is here associated with four non-polar bonds. Quadrivalent tellurium can thus be associated with 54 or with 56 electrons.

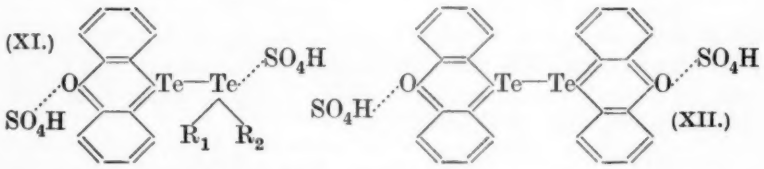
When phenoxtellurine dibisulphate (IX) is treated with hot aqueous barium chloride, it gives 10 : 10-dichlorophenoxtellurine (*loc. cit.*), from which the dibisulphate is regenerated by warming with concentrated sulphuric acid. The latter reaction gives a further general method for the preparation of the dibisulphates of the phenoxtellurine series.

Mechanism of the Development of the Coloured Complex.

A large number of experiments have shown that a coloured complex of this series is developed only by the interaction of a telluride and a salt of the type already indicated. The author considers it probable that the process involves *the migration of an anion from the salt member to the reduced (telluride) member of the pair of generators*, accompanied by union of the two residues.

The salt member (*e.g.*, II) would thus become the "donor" of an acid radical, the reduced member (*e.g.*, I) being the "acceptor." For the sake of brevity, these terms will be employed in the following discussion. The presence of the phenoxtellurine ring system in one member of this pair of generators is essential.

Evidence has been obtained that coloured complexes of the type shown in (XI), in which the right-hand member may be any



organic telluride or sulphide, are capable of existence; but these substances are so readily dissociated that it has hitherto proved impossible to isolate any of them in a pure condition.

Each of the coloured complexes so far obtained in a pure state belongs to the type (XII), in which occur two phenoxtellurine (or substituted phenoxtellurine) rings.

The following table shows the types of substances capable of

producing coloured complexes by interaction with acceptors or donors of the phenoxtellurine series.

Donors.	Acceptors.
Salts of phenoxtellurine, etc.	Phenoxtellurine, etc.
Salts of *cyclo*telluropentanediones.*	*cyclo*Telluropentanediones.
Salts of diethyl sulphide (not isolated).	Tellurodiacetic acid.
Basic tellurium nitrate or sulphate.	Ditellurodiacetic acid.
Concentrated nitric or sulphuric acid.	Diethyl sulphide.
	Hydrogen sulphide.
	Sulphurous acid.
	Base metals (Fe, Cu, Na, etc.).
	1 : 2-Dihydroxybenzenes (pyrogallol).

* The majority of the *cyclo*telluropentanediones can be employed only in the dry way, since the mixed products are decomposed by hot acetic acid with liberation of tellurium. Only the products from 4 : 4-dialkyl*cyclo*telluropentanediones are stable to acetic acid.

The reactions of tellurides with phenoxtellurine dibisulphate afford a very delicate test for the presence of these substances.

These apparently unrelated reactions are unified by adopting the hypothesis that in every case of interaction between a donor and an acceptor there occurs *an exchange of anions from the former for an equal number of electrons from the latter.* The exchange is followed by the union of the two residues with production of the coloured complex, the extent to which this is formed being governed by the prevailing conditions of temperature and concentration as well as by the nature of the interactants.

Substances which act as donors or acceptors but do not themselves enter into the molecule of the resulting complex are intermediary suppliers or receivers of anions. They create donors or acceptors, respectively, of the phenoxtellurine series.

Thus, between diethyl sulphide and phenoxtellurine dibisulphate there is set up the equilibrium :

$$Et_2S + \begin{matrix}SO_4H\\SO_4H\end{matrix}\!\!>\!TeR \rightleftharpoons Et_2S\!<\!\begin{matrix}SO_4H\\SO_4H\end{matrix} + TeR,$$

where R represents the bivalent carbon grouping of phenoxtellurine. Free phenoxtellurine is therefore present in the system and unites with its dibisulphate to give the violet complex, which is in turn in equilibrium with its constituents :

$$\begin{matrix}RTe\text{———}TeR\\ \quad SO_4H\ SO_4H\end{matrix} \rightleftharpoons TeR + \begin{matrix}SO_4H\\SO_4H\end{matrix}\!\!>\!TeR.$$

The two remaining possible complexes, *viz.*,

$$\begin{matrix}RTe\text{———}SEt_2\\ \quad SO_4H\ SO_4H\end{matrix} \text{ and } \begin{matrix}Et_2S\text{———}SEt_2,\\ \quad SO_4H\ SO_4H\end{matrix}$$

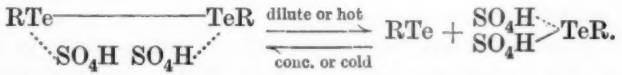
are similarly in equilibrium with their constituents. Naturally, the tendency towards formation of some of the possible complexes

will be small or nil and will in general be governed by the affinities of the active atoms (Te and S in the above case) for anions and by the tendency of these atoms to unite together.

The system in dilute solution is therefore equivalent to one in which there are present in equilibrium only the uncharged substances RTe and Et_2S and the ions $\overset{-}{S}O_4H$,$R\overset{+}{T}e(SO_4H)$ and $Et_2\overset{+}{S}(SO_4H)$.

That this is so has been shown by a variety of experiments; *e.g.*, (i) in the above case, phenoxtellurine dibisulphate becomes violet in gaseous diethyl sulphide; excess of the gas (or presence of liquid diethyl sulphide) changes the colour to red; the violet solid loses diethyl sulphide and becomes pale yellow when removed from the gas. Crystallisation of the violet solid from glacial acetic acid gives only compound (V) in small yield. If phenoxtellurine dibisulphate is exposed on clay to the vapour of diethyl sulphide, a part of it remains permanently violet, showing that a small proportion of $Et_2S(SO_4H)_2$ has been absorbed by the clay, its removal disturbing the normal equilibrium. (ii) The combination of a pair R^1Te and $R^2Te(SO_4H)_2$ gives the same result as that of the reversed pair, R^2Te and $R^1Te(SO_4H)_2$. Thus 4-ethyl*cyclo*telluropentanedione and phenoxtellurine dibisulphate, when combined as solids or in acetic acid, give the same violet complex (IV or V) as does the combination of 4-ethyl*cyclo*telluropentanedione dibisulphate and phenoxtellurine.

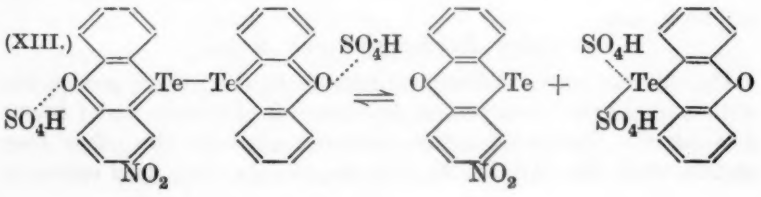
A parallel result occurs when R^1Te and R^2Te represent two different members of the phenoxtellurine series. (iii) The behaviour in glacial acetic acid solution of compound (IV) precisely corresponds with the scheme:



(solution deep cherry-red) (solution pale yellow)

The colour of hot dilute solutions is of the same order of intensity as that of phenoxtellurine alone.

Moreover, when the analogous compound (XIII) is similarly treated, hot dilute solutions show the much enhanced yellow colour due to free 2-nitrophenoxtellurine.



(iv) When a subsidiary reaction can occur to disturb the equilibrium, there is the expected quantitative production of a violet complex. Thus, gaseous or dissolved hydrogen sulphide almost completely converts phenoxtellurine dibisulphate into a violet complex (IV or V), because the intermediate compound $H_2S(SO_4H)_2$ changes rapidly to sulphur and sulphuric acid. Diethyl sulphide, however, has no permanent action, because the corresponding compound $Et_2S(SO_4H)_2$ cannot undergo such a change. Similarly, liquid or gaseous sulphur dioxide has no action upon phenoxtellurine dibisulphate, but the addition of water causes conversion into the violet complex. The compound $SO_2(SO_4H)_2$ is stable; while the hydrated substance, $SO(OH)_2(SO_4H)_2$, undergoes change to sulphur trioxide and sulphuric acid. It is not suggested that compounds such as $SO_2(SO_4H)_2$ are present in more than a minute proportion. The smallest proportion would suffice were the compound immediately removed by a subsidiary reaction.

The reverse phenomenon is seen in the action of sulphuric and nitric acids upon phenoxtellurine. The acids supply anions to tellurium in exchange for electrons, leaving nascent (uncharged) hydrogen, which is removed by its subsidiary reducing action upon the excess of acid.

Reducing agents are thus pictured as those which can supply electrons and receive anions, oxidising agents receiving electrons and supplying anions. (Compare the oxidising action of nitrous acid upon phenoxtellurine, see p. 3057, in which hyponitrous acid or nitric oxide is doubtless formed.)

Some of the phenomena seem to suggest that acceptors in solution are to some extent separated from their unshared valency electrons (extra-valency electrons).

It is suggested that basic tellurium nitrate, which is known to have the empirical formula $2TeO_2,HNO_3$, has the structure $OTe<^{O}_{O}>Te<^{OH}_{NO_3}$, and that the donor prepared by the author from tellurium tetrachloride and concentrated sulphuric acid is the analogous bisulphate or dibisulphate.

In the case of *o*-dihydroxybenzenes (pyrogallol), the oxygen atoms probably receive the anions, which are immediately removed by a subsidiary reaction, such as the formation of *o*-quinones and sulphuric acid.

Colour Development with Metals.

On rubbing phenoxtellurine dibisulphate (IX) upon porous tile with a steel knife, a surprising development of intense violet colour was noted. The same action occurred with all the other base metals tried (Na, Al, Fe, Ni, Cu, Zn, Sn, As, Sb), used either in

the form of polished strips or as powder, but no effect was produced with the noble metals (Ag, Pt, Au, and also Hg); sulphur and tellurium were also devoid of action. The reaction can therefore be used to distinguish base from noble metals.

The members of the phenoxtellurine dinitrate series behave generally in the same manner, but the corresponding salts of those tellurides which do not contain a phenoxtellurine ring produce no colorations with the metals.

The base metals exhibit selective action towards different anions. Iron, for example, produces a coloration with both dinitrate and dibisulphate of phenoxtellurine; copper or nickel, only with the latter salt. These reactions therefore afford a rough indication of the relative attractions of different metals for certain anions.

The base metals do not enter into the molecule of the violet substances which they produce in this manner. The action of the metallic particles is to remove anions, in exchange for electrons, from the salt molecules, forming free phenoxtellurine, which then combines with unchanged salt to produce substances (IV) and (V). Salts of the metals are thus present in equilibrium with the violet tellurium compounds, and in the case of the dibisulphate the balance is controlled by the proportion of water present. This is rendered visible in the action of iron upon phenoxtellurine dibisulphate, for the violet mixture becomes red when dried on clay in a desiccator, but the violet colour is restored on exposure to moist air. In this alternation, which can be repeated indefinitely, the red stage denotes the presence of compound (III), and the violet that of compound (IV) or (V). The hydrated iron sulphate or basic sulphate present must therefore have a greater affinity for sulphuric acid than the corresponding anhydrous iron salt, the affinity of compound (IV) for sulphuric acid being intermediate between these two values. When nickel is substituted for iron, reversibility is no longer manifest, the violet stage being permanent.

The above view of the action of base metals upon the salts of phenoxtellurine is supported by the fact that the violet mixtures produced by the action of such metals are decomposed by water with liberation of "free" phenoxtellurine, which is obtained in a pure state by extraction with ether.

Pairs containing Mixed Nuclei.

A preliminary study has been made of the action between phenoxtellurine dibisulphate and 2-nitrophenoxtellurine. The violet-blue product, when crystallised from glacial acetic acid, was found to be a mixture of the complex derived from 2-nitrophenoxtellurine with the salt of phenoxtellurine, together with a much smaller

proportion of the complex derived from phenoxtellurine and its salt. 2-Nitrophenoxtellurine did not occur as a donor, two of the possible four coloured complexes being thus eliminated. The reversed pair (2-nitrophenoxtellurine dibisulphate and phenoxtellurine) gave an exactly similar product.

The tellurium atom in phenoxtellurine has thus a much greater affinity for bisulphate radicals than has that in 2-nitrophenoxtellurine.

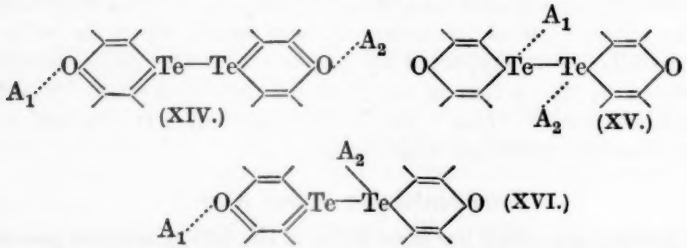
This behaviour affords a means of pitting, as it were, two differently combined tellurium atoms against one another in contest for a series of anions, and enables, for example, the effect of different ring substituents upon the electropositiveness of the tellurium atom in phenoxtellurine to be assessed.

The method of examining a coloured complex consists in treating it with water, when the acceptor is set free and can be extracted by ether; the residual salt can then be reduced by adding potassium bisulphite, and the nucleus of the donor again extracted by ether. The products are insoluble in water, so that fresh equilibria cannot presumably be set up.

The addition of a molecular proportion of phenoxtellurine dibisulphate, which is insoluble in ether, to 2 : 4-diethyl*cyclo*telluropentanedione dissolved in ether led to the precipitation of blue complexes and the rapid removal of the *cyclo*telluropentanedione from solution, its place being supplied by free phenoxtellurine. The tellurium atom of this *cyclo*telluropentanedione has therefore a much greater affinity for bisulphate radicals than has that of phenoxtellurine.

These methods should yield results of value in the study of the polarity of groups.

Colour production among the tellurylium compounds is ascribed to the occurrence of the structure (XIV), in which A_1 and A_2



represent HSO_4, ClO_4, NO_3, H_2PO_4, or OH radicals; but it should be pointed out that structures (XV) and (XVI) are possible alternatives. Again, tellurium might conceivably be joined to "oxonium" oxygen, or the two oxygen atoms might be united. These

formulæ, however, do not reflect so well as (XIV) the fact that the presence of the phenoxtellurine ring is essential, such substances as diphenyl ether yielding no coloured complexes.

The reason why A_1 and A_2 cannot represent Cl, Br, or $CH_3{\cdot}CO{\cdot}O$ is probably the very small tendency of these radicals to ionise when united with tellurium. The tendency nevertheless exists, for reduction is possible in these instances when a subsidiary reaction can occur.

It is noteworthy that each of the mobile acid radicals possesses doubly-bonded oxygen. The nitrate ion appears to be mobile even in reaction between dry solids (phenoxtellurine and its anhydrous dinitrate).

Phenothioxin, which gives an intensely violet solution in concentrated sulphuric acid, probably forms a series of coloured salts, and it is hoped to apply to that problem the experimental methods developed in the present paper. The foregoing principles have also possible application in many other directions. The author desires to reserve for the present the study of this subject.

Experimental.

Phenoxtellurine 10 : 10-*dinitrate* (II), large, colourless needles or glistening plates, m. p. 258° (efferv.), was prepared by crystallising phenoxtellurine (1 g.) from nitric acid (105 c.c., made by diluting 2 vols. of the concentrated acid with 1 vol. of water). It is stable in moist air, but is slowly hydroxylated by water (Found : C, 34·4; * H, 2·0.* $C_{12}H_8O_7N_2Te$ requires C, 34·3; H, 1·9%).

The following were similarly prepared from the nitro-derivatives of phenoxtellurine :

2-*Nitrophenoxtellurine* 10 : 10-*dinitrate* formed minute, colourless needles, m. p. 196—197° (efferv.), from dilute nitric acid and was slowly decomposed by moist air (Found : N, 8·2.* $C_{12}H_7O_9N_3Te$ requires N, 9·1%).

2 : 8-*Dinitrophenoxtellurine* 10 : 10-*dinitrate* crystallised from concentrated nitric acid in large, colourless, serrated needles, m. p. 259° (efferv.). It was slowly decomposed by moist air (Found : N, 10·0.* $C_{12}H_6O_{11}N_4Te$ requires N, 11·0%).

When a 4-nitro-group was present in the phenoxtellurine ring, basic nitrates appeared to be produced, for which the following constitutions are conjectured :

4-*Nitro*-10-*hydroxyphenoxtellurine* 10-*nitrate monohydrate* crystallised from dilute nitric acid in minute, white rods, m. p. 243° (decomp.) (Found : N, 6·3.* $C_{12}H_{10}O_8N_2Te$ requires N, 6·4%).

4 : 8-*Dinitro*-10-*hydroxyphenoxtellurine* 10-*nitrate monohydrate*

* Indicates a figure obtained by micro-analysis.

separated from concentrated nitric acid in small, white needles, which decomposed violently at 237—239° (Found: C, 30·4*; H, 1·9*; N, 8·9,* 9·1,* 9·2.* $C_{12}H_9O_{10}N_3Te$ requires C, 29·9; H, 1·9; N, 8·7%).

Reduction of the above nitrates and basic nitrates showed that further nitration of the nucleus had not occurred during the treatment with nitric acid.

Note.—The micro-Dumas method of analysis for nitrogen, which was employed to obtain the above figures, appears to give results which are only approximate for tellurium compounds containing nitrate groups. The results are recorded, therefore, merely for reference. The method is accurate when applied to tellurium compounds containing the whole of the nitrogen in the form of nitro-groups.

The nitrates were unaffected by liquid sulphur dioxide, but the addition of a trace of water to the mixture caused in several cases the instant development of a violet colour, which changed to the yellow or orange of the reduction product on the addition of more water. The permanence and intensity of the violet coloration varied among different members of the series.

The following phenomena were noted on rubbing together between glass surfaces the substances indicated:

Acceptor.	Donor (in form of nitrate or basic nitrate).	Colour produced.
Phenoxtellurine.	Phenoxtellurine.	Intense violet.
2-Nitrophenoxtellurine.	Phenoxtellurine.	,, ,,
Phenoxtellurine.	2 : 8-Dinitrophenoxtellurine.	Feeble violet.
2-Nitrophenoxtellurine.	2-Nitrophenoxtellurine.	Rather feeble violet.
2 : 8-Dinitrophenoxtellurine.	Phenoxtellurine.	None.
2 : 8-Dinitrophenoxtellurine.	2 : 8-Dinitrophenoxtellurine.	None.
Phenoxtellurine.	4 : 8-Dinitrophenoxtellurine.	Intense violet.
4 : 8-Dinitrophenoxtellurine.	4 : 8-Dinitrophenoxtellurine.	None.

These results clearly indicate the inhibitory effect of an accumulation of nitro-groups upon the ease of development of the coloured compounds, especially when the nitro-groups are in the 2- and 8-positions (*i.e.*, meta- to the tellurium atom). That this effect is due less to a depression of mobility of the nitrate ion than to a depression of receptiveness in the tellurium atom of the acceptor is shown by the fact that the effect is greater when the nitro-groups are in the acceptor than when they are in the donor of the same pair. In other words, the presence of nitro-groups in the acceptor depresses the mobility of the electron available for exchange.

Diphenoxtellurylium dibisulphate disulphuric acid trihydrate (III) was prepared by the following methods: (1) *Action of sulphuric*

* Indicates a figure obtained by micro-analysis.

acid on phenoxtellurine. Phenoxtellurine (6 g.) was dissolved in concentrated sulphuric acid (40 c.c.), and the intensely red solution kept for ½ hour, sulphur dioxide escaping. The liquid was then cooled in ice and salt, and water (25 c.c.) gradually stirred in. After about an hour, the red crystals were filtered off through sintered glass and kept on porous tile in a desiccator. The same substance was produced when 1·1 g. of phenoxtellurine was treated with 15 c.c. of concentrated sulphuric acid and 10 c.c. of water. The yield is about 94% of the theoretical [Found : C, 27·5; H, 2·9; O, 32·5 (by diff.); S, 12·6; Te, 24·5. $C_{24}H_{28}O_{21}S_4Te_2$ requires C, 27·8; H, 2·7; O, 32·5; S, 12·4; Te, 24·6%]. The red crystals were hygroscopic, becoming moist with sulphuric acid and gaining about 30% of their weight of water when exposed to air for several days in a glass dish. When exposed on clay, the substance lost sulphuric acid and was transformed quantitatively into the greenish-violet compound (IV). Gaseous ammonia occasioned a similar change. When the red crystals (0·544 g.) were treated with cold water (15 c.c.), decomposition ensued and phenoxtellurine (0·13 g.; calc., 0·155 g.) became extractable by ether. The residue, after reduction by aqueous potassium bisulphite, gave a further molecular proportion of phenoxtellurine (0·155 g.; calc., 0·155 g.). The red crystals had no definite melting point, becoming slowly blue-black near 100° and decomposing indefinitely near 165° to a black mass which became violet above about 235° but did not melt.

(2) Phenoxtellurine was dissolved in glacial acetic acid, and a considerable proportion of concentrated sulphuric acid containing a little water added; the red crystals separated on keeping.

(3) When either of the violet substances (IV and V) was treated with sulphuric acid containing a little water, or with acetic-sulphuric acid, the red crystals were produced, provided the concentration of sulphuric acid was sufficiently high.

(4) The same result was obtained by mixing phenoxtellurine and its hydrated dibisulphate (IX) in glacial acetic acid and adding a little concentrated sulphuric acid.

Diphenoxtellurylium hydroxybisulphate monohydrate (V) was prepared (1) by dissolving phenoxtellurine in warm glacial acetic acid and adding a few drops of concentrated sulphuric acid, the intensely coloured solution crystallising on cooling; (2) by crystallising the red substance (III) or the greenish-violet substance (IV) several times from glacial acetic acid, with filtration through sintered glass, if necessary; (3) by warming together, in glacial acetic acid, phenoxtellurine and its hydrated dibisulphate (IX) and recrystallising the product from glacial acetic acid; (4) by dissolving phenoxtellurine in concentrated sulphuric acid, cautiously stirring in water until

the solution began to deposit a blue precipitate, allowing it to stand, and then collecting the precipitate and crystallising it from glacial acetic acid; (5) by grinding together phenoxtellurine and its hydroxybisulphate or dibisulphate and recrystallising the product from glacial acetic acid.

The product forms copper-coloured flakes or rosettes of needles giving a violet-black powder. It has no definite melting point, losing colour gradually at 205—245° and forming phenoxtellurine and a whitish solid which is unmelted at 300°. Heated at 100° in a vacuum, it does not lose its molecule of combined water. The change on heating represents a decomposition into phenoxtellurine and its hydroxybisulphate, since partial redevelopment of violet colour occurs on cooling and grinding the whitish mixture.

The compound is decomposed only slowly by ether and other organic solvents (contrast the similar substances containing nitrate radicals, which are decomposed much more rapidly), but it is quickly disrupted by cold water; *e.g.*, 0·404 g., on being shaken with 10 c.c. of water, generated a molecular proportion of free phenoxtellurine (0·186 g.; calc., 0·166 g.), which was extractable by ether [Found: C, 39·7, 39·6, 39·6; H, 2·6, 2·5, 2·9; O, 17·5 (by diff., in a single sample); S, 4·0, 4·9; Te, 35·1. $C_{24}H_{20}O_8STe_2$ requires C, 39·8; H, 2·8; O, 17·7; S, 4·4; Te, 35·25%].

When pure, the substance gives in hot glacial acetic acid a clear solution which is colourless when dilute and intensely cherry-red when concentrated. Cold solutions are much more coloured than hot solutions of the same concentration. Solutions in glacial acetic acid immediately reduce anhydrous ferric chloride. The compound dissolves in syrupy phosphoric acid to an intensely blue solution.

Diphenoxtellurylium dibisulphate di- or *tri-hydrate* (IV) is best prepared by leaving the powdered red substance (III) on porous tile in moist air for a few days, with occasional turning. A deep bluish-black, stable, crystalline powder, with greenish reflex, remains. It may also be prepared by any of the methods indicated for the hydroxy-compound (V), if the product be crystallised finally from glacial acetic acid containing a little concentrated sulphuric acid (too great a proportion of sulphuric acid leads to the production of III). Two different samples were prepared by the first method, one being apparently a di- and the other a tri-hydrate; the difference is probably due to a slight variation in the conditions during drying [Found, for sample prepared by transforming V to III and then exposing this to air and finally drying it on clay in a desiccator during 2 days: C, 34·5; H, 2·9. $C_{24}H_{24}O_{13}S_2Te_2$ (the trihydrate) requires C, 34·35; H, 2·85%. Found, for sample

prepared by crystallising III from glacial acetic acid containing 4% by volume of concentrated sulphuric acid, and then exposing the product on clay and finally drying it in a vacuum over sulphuric acid during 12 hours: C, 35·3; H, 2·8; O, 22·9 (by diff.); S, 7·3; Te, 31·7. $C_{24}H_{22}O_{12}S_2Te_2$ (the dihydrate) requires C, 35·1; H, 2·7; O, 23·3; S, 7·8; Te, 31·05%]. The dihydrate seemed slowly to absorb moisture when exposed to the air. Both the di- and the tri-hydrate were decomposed by cold water, first into sulphuric acid and compound (V), and finally into phenoxtellurine and its basic bisulphate.

Phenoxtellurine 10 : 10-*Diacetate* (VI).—A solution of phenoxtellurine in hot glacial acetic acid was allowed to cool and then aqueous hydrogen peroxide was stirred in drop by drop until the yellow colour of the solution was discharged. The solution was heated to boiling and treated with sufficient water to produce a faint turbidity; the diacetate slowly separated in long, colourless needles. Concentration of the mother-liquor gave a further crop, the total yield being more than 90% of the theoretical. The substance is soluble in hot water with hydrolysis, sparingly soluble in ether or petroleum, and easily soluble in hot benzene, from which it crystallises readily. It gave no coloration when ground with phenoxtellurine or with metals (Found: C, 46·5; H, 3·4. $C_{16}H_{14}O_5Te$ requires C, 46·4; H, 3·4%). The diacetate melts with effervescence at 205—207°. It is readily reduced to phenoxtellurine by aqueous alkali bisulphites.

Phenoxtellurone, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>TeO_2$.—When phenoxtellurine is dissolved in acetone and treated with an excess of 30% aqueous hydrogen peroxide, a white, amorphous precipitate is thrown down. The same result occurs if an excess of hydrogen peroxide be used in the preparation of phenoxtellurine diacetate. The substance, which is insoluble in water or acetone but soluble in hot glacial acetic acid, is reduced to the tellurous state by concentrated sulphuric or hydrochloric acid, oxygen or chlorine being evolved with production of a salt of phenoxtellurine. Hydriodic acid promotes a similar reduction, with liberation of iodine. The product is insoluble in dilute mineral acids but is soluble in aqueous caustic alkali. After heating in a vacuum at 110° during an hour, it had the composition of the half-anhydride of the semi-ortho-form of the tellurone, *viz.*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>Te(O)(OH)\cdot O\cdot(OH)(O)Te<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>O$ (Found: C, 42·5; H, 2·7. $C_{24}H_{18}O_7Te_2$ requires C, 42·8; H, 2·7%).

Sulphates of Phenoxtellurine.—Phenoxtellurine 10 : 10-diacetate (7·1 g.) was heated with 300 c.c. of water, nearly all dissolving.

To the hot solution was added a mixture of 100 c.c. of water and 100 c.c. of concentrated sulphuric acid, and the whole was heated to the boiling point. The clear solution obtained, on cooling, gave 6·5 g. of cream-coloured crystals.

Portions of this substance were then crystallised from sulphuric acid of various concentrations, and the products examined: (i) The material was dissolved in a large volume of boiling water, and to the cold solution a minimum of sulphuric acid was added to effect separation of crystals. The liquid slowly deposited *phenoxtellurine sulphate* (VII) in thin, almost colourless, very refractive needles, which became slightly cream-coloured on drying on clay in a vacuum during a day (Found: C, 36·5, 36·7; H, 2·4, 2·5. $C_{24}H_{16}O_{10}S_2Te_2$ requires C, 36·8; H, 2·05%). This substance developed only a trace of colour when ground with phenoxtellurine.

(ii) The material was dissolved in a boiling mixture of 1 vol. of concentrated sulphuric acid and 1·22 vols. of water. Voluminous cream-coloured flakes separated, and these, after being drained on clay and then heated during 5 hours at about 115° in a vacuum (loss = 2·4%), gave analytical figures which corresponded with a mixture or *compound* containing two molecular proportions of phenoxtellurine hydroxybisulphate (VIII) and one of phenoxtellurine dibisulphate, together with a molecule of water [Found: C, 32·3, 32·35; H, 2·6, 2·6; O, 26·5 (by diff.); S, 9·4; Te, 29·1. $C_{36}H_{32}O_{22}S_4Te_3$ requires C, 32·55; H, 2·4; O, 26·5; S, 9·65; Te, 28·8%]. The substance gave a violet colour when ground with phenoxtellurine. Its solution in concentrated sulphuric acid was orange-red.

(iii) When the material was dissolved, with gentle warming, in concentrated sulphuric acid (1·7 g. to 10 c.c. of acid) and the clear orange-red solution treated with the minimum of water (about 1 c.c.) sufficing to cause slow separation of crystals, bright yellow, glistening plates were obtained. When filtered off rapidly through sintered glass and drained on clay in a vacuum, the crystals changed to a creamy-yellow powder of *phenoxtellurine dibisulphate trihydrate* (IX) [Found: C, 26·4; H, 3·0; O, 34·5 (by diff.); S, 12·2; Te, 23·9. $C_{12}H_{16}O_{12}S_2Te$ requires C, 26·5; H, 2·9; O, 35·3; S, 11·8; Te, 23·5%]. The substance gave an intense violet coloration with phenoxtellurine and other tellurides, or with iron and other base metals. Its solution in sulphuric acid became intensely red-brown on addition of hydrogen peroxide.

Each of the above sulphates of phenoxtellurine, when reduced by alkali bisulphite, gave phenoxtellurine as the sole organic product, showing that in no case had nuclear sulphonation occurred.

Note on the Analysis of Aromatic Tellurium Compounds containing

Sulphur.—It was found necessary, in determining sulphur and tellurium in the same sample, to adopt the following procedure: The sample was heated with fuming nitric acid during 24 hours at 250—280° in a Carius tube, the contents of the tube dissolved in about 100 c.c. of concentrated hydrochloric acid, and the solution evaporated to a few c.c. on the water-bath. The residue was taken up in dilute hydrochloric acid (about 200 c.c.), with filtration from traces of glass or silica if necessary. Sulphur was estimated by digestion during 12 hours with a slight excess of barium chloride. The liquid (filtrate from barium sulphate) was then freed from excess of barium by digesting it similarly with a slight excess of sulphuric acid and evaporated completely on the water-bath, and tellurium was estimated in the residue by the usual method.

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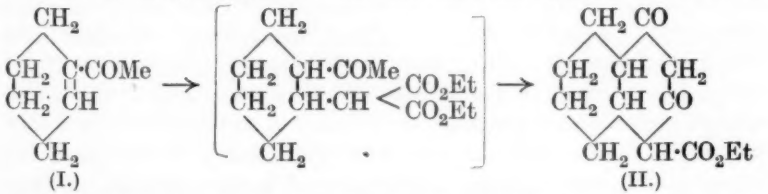
[*Received, September 14th,* 1926.]

CCCCX.—*Preparation of* cis-o-*Carboxy*cyclo*hexaneacetic Acid.*

By GEORGE ARMAND ROBERT KON and MUHAMMAD QUDRAT-I-KHUDA.

cis-*o*-CARBOXY*cyclo*HEXANEACETIC acid was first obtained by Windaus, Hückel, and Reverey (*Ber.*, 1923, **56**, 91), by a somewhat laborious method, as a mixture of *cis*- and *trans*-forms not easy to separate. This difficulty was partly overcome by Dutt (unpublished work), who obtained the pure *trans*-form by condensing ethyl Δ^1-*cyclo*hexenecarboxylate with ethyl cyanoacetate and hydrolysing the product. A method for the preparation of the pure *cis*-form has now been devised.

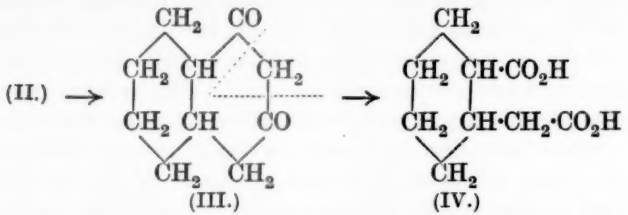
*cyclo*Hexenyl methyl ketone (I) readily condenses with ethyl sodiomalonate (compare Kon, this vol., p. 1792), giving *ethyl* 1 : 3-*diketodecahydronaphthalene*-4-*carboxylate* (II). This ester, on alkaline hydrolysis, passes into the diketone (III), which is in



(I.) (II.)

every way analogous to dimethyldihydroresorcinol and other well-known compounds of the same series. It is readily oxidised by alkaline hypobromite with formation of *cis*-*o*-carboxy*cyclo*hexaneacetic

acid (IV), whereas the action of permanganate gives *trans-cyclo*hexane-1 : 2-dicarboxylic acid.



The yields are good throughout, although some difficulty is experienced in the preparation of *cyclo*hexenyl methyl ketone by Darzens's method (*Compt. rend.*, 1910, **150**, 707).

EXPERIMENTAL.

*cyclo*Hexenyl methyl ketone was prepared by the action of acetyl chloride on *cyclo*hexene in the presence of tin tetrachloride (Darzens, *loc. cit.*); the yield of ketone did not exceed 40% owing to the formation of resinous by-products.

The ketone (49 c.c.) was added to ethyl sodiomalonate, prepared from 64 c.c. of the ester and 10 g. of sodium in 140 c.c. of alcohol, and the mixture was heated on the steam-bath for 4 hours and kept over-night. Water was then added, neutral impurities removed with ether, the solution strongly acidified, and the precipitated oil taken up in ether. On removing the solvent, an oil was obtained which gradually solidified and crystallised well from ether–petroleum in needles, m. p. 114°, consisting of the *ester* (II). The yield was 80 g. or 60% (Found : C, 65·5; H, 7·6. $C_{13}H_{18}O_4$ requires C, 65·5; H, 7·6%). The compound is readily soluble in the usual organic solvents except petroleum and has the usual properties of compounds of this class; with ferric chloride it gives a brown colour which becomes redder and more intense on standing.

The keto-ester was hydrolysed with boiling aqueous barium hydroxide, but the product was liquid, probably owing to partial ring fission. With alcoholic potassium hydroxide the hydrolysis proceeded smoothly. The ester (24 g.) was heated over-night with 170 c.c. of 20% alcoholic alkali and the solution was diluted, extracted with ether, and acidified. On extraction with ether, an oil was obtained which gradually solidified; it was boiled with water, to which a little mineral acid had been added, to complete the removal of carbon dioxide. The *diketone* (III) crystallised as a yellow solid on cooling and formed needles, m. p. 142°, from dilute alcohol (yield, 60%) (Found : C, 71·9; H, 8·3. $C_{10}H_{14}O_2$ requires C, 72·2; H, 8·4%). With ferric chloride, it gives a brown coloration.

The diketone (III) (4 g.), dissolved in 10 c.c. of ice-cold 10% sodium hydroxide solution, was gradually added with shaking to an ice-cold hypobromite solution prepared from 6 g. of bromine neutralised with 10% aqueous sodium hydroxide (200 c.c.) and kept for ¾ hour. The precipitated bromoform was extracted with ether, the excess of bromine destroyed with sulphur dioxide, and the solution acidified with sulphuric acid and extracted with ether. The crude acid obtained, after several crystallisations from water, melted at 146—147° and was shown to consist of pure *cis-o*-carboxy-*cyclo*hexaneacetic acid by the ready formation of the anhydride, m. p. 57°, on treatment with acetyl chloride (Found: C, 58·0; H, 7·4. Calc.: C, 58·1; H, 7·5%. Found in the disilver salt: Ag, 53·9. Calc.: Ag, 53·9%).

No *trans*-acid was isolated from the mother-liquors from the crystallisation of the *cis*-acid, although small quantities may have been present.

The diketone (4 g.), dissolved in 10 c.c. of 10% aqueous sodium hydroxide, was added to 260 c.c. of 5% potassium permanganate solution. After 48 hours, the excess of this reagent was destroyed with sulphur dioxide and the solution was acidified with sulphuric acid and extracted with ether. The extract on evaporation gave *trans-cyclo*hexane-1 : 2-dicarboxylic acid, m. p. 222° after recrystallisation from water (Found: C, 55·6; H, 7·0. Calc.: C, 55·8; H, 7·0%. Found in the disilver salt: Ag, 55·6. Calc.: Ag, 55·8%).

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, September 30th*, 1926.]

CCCCXI.—*Co-ordinated Mercaptides.*

By ALAN MACLEAN DRUMMOND and DAVID TEMPLETON GIBSON.

MANY investigations have been undertaken to determine which of the formulæ $R{\cdot}SO_2{\cdot}SR$ (I) and $R{\cdot}SO{\cdot}SO{\cdot}R$ (II) better represents the reactions of disulphoxides. Hilditch (J., 1910, **97**, 1091), who examined the rotations of camphor disulphoxide and related substances, supported (II), whereas the recent work of Smiles (J., 1924, **125**, 176; 1925, **127**, 224) is decidedly in favour of (I).

Our original aim was to prepare *d*-camphoryl *l*-camphoryl disulphoxide, for according as this substance is (I) or (II) it should be

$$(d)C_{10}H_{15}O{\cdot}SAg + Cl{\cdot}SO_2{\cdot}C_{10}H_{15}O(l) = AgCl + (d)C_{10}H_{15}O{\cdot}S{\cdot}SO_2{\cdot}C_{10}H_{15}O(l) \text{ or } (d)C_{10}H_{15}O{\cdot}SO{\cdot}SO{\cdot}C_{10}H_{15}O(l)$$

optically active or internally compensated; but all our attempts were unsuccessful. We eventually traced the failure to the fact

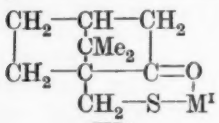
that the silver derivative of thiolcamphor is not a normal mercaptide, but has the composition $C_{10}H_{15}O{\cdot}SAg,AgNO_3,H_2O$ (A); and only one-half of the silver is ionised in aqueous alcohol. It is readily soluble in benzene containing thiolcamphor and from the resulting orange-red solution a yellow solid was obtained in which one-third of the silver is ionisable.

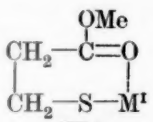
$$3C_{10}H_{15}O{\cdot}SAg,AgNO_3,H_2O + C_{10}H_{15}O{\cdot}SH = 2(C_{10}H_{15}O{\cdot}SAg)_2,AgNO_3,H_2O + HNO_3 + H_2O.$$

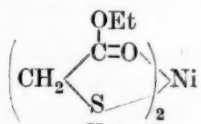
The substance depressed the freezing point of benzene so slightly that it was thought desirable to test the solution for colloidality; but neither Tyndall cone nor Brownian movement was observed and a solution in benzene diffused rapidly through parchment. The nickel derivative (B), $(C_{10}H_{15}O{\cdot}S)_2Ni,C_{10}H_{15}O{\cdot}SH$, is a mahogany coloured powder, very soluble in benzene.

These remarkable properties—non-ionisable character, solubility in anhydrous organic solvents, anomalous colour, and, in certain cases, stability on heating—support the view that the metallic atom is combined, not only with the sulphur atom of the thiolcamphor complex (III) by a principal valency, but also with the carbonyl group by residual affinity (compare the acetylacetone derivatives; Morgan and Moss, J., 1914, **105**, 189).

Recent work on the constitution of Reychler's acid (Wedekind, Schenk, and Stüsser, Ber., 1923, **56**, 633; Burgess and Lowry, J., 1925, **127**, 271) indicates that thiolcamphor is probably a β-thiol ketone. The co-ordinated ring structure of thiolcamphor derivatives, therefore, is six-membered, as with the β-diketones, nitroso-β-naphthol, etc., discussed by Sidgwick and Callow (J., 1924, **125**, 533). The new compounds differ from these in not having conjugated double bonds.


(III.)


(IV.)


(V.)

We have also examined methyl β-thiolpropionate, as it is the simplest compound containing the group we consider responsible for the abnormal behaviour of thiolcamphor derivatives. Its metallic derivatives (see IV) show similar abnormalities. The silver compound (C), $AgS{\cdot}C_4H_7O_2,AgNO_3,H_2O$, is, however, only sparingly soluble in a solution of the parent ester. The nickel derivatives of methyl β-thiolpropionate and of ethyl thiolacetate (V) are brown and crystalline and are very soluble in benzene, but, unlike (B), they do not contain an extra molecule of the mer-

captan. The five-membered ring compound seems to be more stable than the six-membered ones, for, whereas the other nickel compounds soften gradually on heating, (V) melts sharply without decomposition like Sidgwick and Plant's co-ordination compounds of the alkali metals (J., 1925, **127**, 209).

The metallic derivatives of hydroxymethylenecamphor prepared by Lifschitz (*Rec. trav. chim.*, 1922, **41**, 627) are probably similar in constitution to the preceding. On the other hand, nickel β-thiolpropionate is similar to the previous compounds only in colour, and nickel thiolacetate is dirty green.

These experiments were rendered possible by the discovery that Lowry and Donington's original method (J., 1903, **83**, 480) for preparing thiolcamphor from the sulphonyl chloride is very materially improved by first reducing the chloride to the sulphinic acid and then reducing this to the mercaptan.

Experimental.

Thiolcamphor.—Camphorsulphonyl chloride was reduced to the sulphinic acid in the way described by Hilditch (J., 1910, **97**, 1096) except that no acetone was used as solvent. The oily sulphinic acid (12 g.) was added cautiously to a vigorously boiling mixture of granulated tin (20 g.) and concentrated hydrochloric acid (500 c.c.), and the whole immediately steam-distilled. The mercaptan, which solidified in the condenser (yield, 5 g.), was contaminated with a small quantity of a volatile tin compound, which was removed by two crystallisations from spirit. The mercaptan was obtained as cubic crystals and as needles, each form melting at 66°. Much poorer yields were obtained with zinc, aluminium, magnesium, or nickel in place of tin.

Silver Thiolcamphor Argentinitrate (A).—Thiolcamphor (5 g.) in alcohol (50 c.c.) was added to silver nitrate (11 g.) in 90% alcohol (100 c.c.) with stirring. A yellow precipitate momentarily formed and dissolved again. Kept in subdued light, the solution slowly deposited white crystals (14 g.) [Found: C, 25·2; H, 3·6; S, 7·1; N, 3·2; Ag (total), 45·1; Ag (ionised), 22·6. $C_{10}H_{17}O_5NSAg_2$ requires C, 25·1; H, 3·6; S, 6·7; N, 2·9; Ag (total), 45·1; Ag (ionised), 22·6%]. The compound chars at 200—210°, and in chloroform solution has $[\alpha]^{19°}_{5461}$ + 21°. It is soluble in ethylene dibromide and in hot alcohol, but insoluble in benzene and ligroin. This and the following compound gave the brown-ring test for nitrate.

The orange-red solution obtained by warming 2 g. of (A) for a few minutes with a solution of thiolcamphor (0·8 g.) in dry benzene (12 c.c.) was separated from the water formed, concentrated in a

vacuum, and poured into ligroin (50 c.c.). The precipitated yellow solid (80% yield) decomposed above 230° without melting. It is extremely readily soluble in benzene, less soluble in alcohol, and has $[\alpha]_{5461}^{18°}$ + 64° in chloroform solution [Found: C, 31·8; H, 4·1; S, 8·2; N, 1·6; Ag (total), 41·8; Ag (ionised), 13·5. $C_{20}H_{32}O_6NS_2Ag_3$ requires C, 31·2; H, 4·2; S, 8·3; N, 1·8; Ag (total), 42·1; Ag (ionised), 14·0%].

Thiolcamphor Cadmibromide.—Crystalline cadmium bromide (0·8 g.) dissolved in alcohol was added to a similar solution of thiolcamphor (0·4 g.). The *cadmibromide* separated immediately in fine, white crystals insoluble in all the usual solvents (Found: Cd, 29·3; Br, 21·8. $C_{10}H_{15}OBrSCd$ requires Cd, 30·0; Br, 21·4%).

Thiolcamphor Stannochloride.—A filtered solution of stannous chloride (0·4 g.) in dry ether was added to thiolcamphor (0·3 g.) in the same solvent. The *stannochloride* separated over-night as glistening crystals, soluble in benzene and other organic solvents; m. p. 187° without decomp. [Found: Sn, 25·8; Cl, 15·8 (by Robertson's method, J., 1915, **107**, 902); S, 10·3; H, 4·9. $(C_{10}H_{16}OS)_3,Sn_2Cl_4$ requires Sn, 25·7; Cl, 15·4; S, 10·4; H, 4·9%].

Nickel Thiolcamphor (B).—Thiolcamphor (0·4 g.) in alcohol was added to a solution of nickel chloride (0·8 g.) and sodium acetate (0·4 g.) in aqueous alcohol. The deep red solution was evaporated in a vacuum and extracted with benzene. Evaporation of this solution gave a mahogany-coloured solid soluble in all the usual organic solvents, but insoluble in water (Found: Ni, 9·4; S, 15·5. $C_{30}H_{46}O_3S_3Ni$ requires Ni, 9·7; S, 15·8%).

Cupric chloride, like ferric chloride, oxidises thiolcamphor to the disulphide, m. p. 222°.

Methyl β-thiolpropionate, prepared by esterifying β-thiolpropionic acid with methyl alcohol and a few drops of concentrated sulphuric acid, is a colourless, mobile, pungent liquid, b. p. 54—55°/14 mm.; $n^{19°}$ 1·4628 (Found: S, 26·3. $C_4H_8O_2S$ requires S, 26·6%).

Methyl silver β-thiolpropionate argentinitrate was prepared as (A) above, and is similar to it in properties (Found: Ag, 52·4; S, 8·0. $AgC_4H_7O_2S,AgNO_3,H_2O$ requires Ag, 52·0; S, 7·7%). The compound gives a positive brown-ring test.

Methyl nickel β-thiolpropionate, prepared as (B), was obtained in brown, rhombic plates after crystallisation from ether [Found: Ni, 19·7; S, 21·3. $(C_4H_7O_2S)_2Ni$ requires Ni, 19·9; S, 21·5%].

Ethyl nickel thiolacetate was obtained in good yield in dark brown, lustrous needles after crystallising from benzene–ligroin. These crystals smelt faintly of the ester. This smell was easily removed by heating for a short time in a high vacuum at 70°. The com-

pound then melted sharply at 101°, without decomposition, to a clear brown liquid [Found: Ni, 20·0; S, 21·0. $(C_4H_7O_2S)_2Ni$ requires Ni, 19·9; S, 21·5%].

Nickel thiolpropionate is a brown powder soluble in dilute alkali, reprecipitated by acid, and insoluble in organic solvents [Found: Ni, 22·3. $(C_3H_5O_2S)_2Ni$ requires Ni, 21·9%].

Under the same conditions nickel chloride and thiolacetic acid gave a dirty green solid of variable composition (Found: Ni, 28·4, 29·1; S, 11·2%).

UNIVERSITY OF GLASGOW. [*Received, October 8th*, 1926.]

CCCCXII.—*The Constituents of Oil of Supa. A New Natural Source of Copaene.*

By GEORGE GERALD HENDERSON, WILLIAM M'NAB, and JOHN MONTEATH ROBERTSON.

OIL of supa from the tree *Sindora Wallichii*, Benth, which is widely distributed over the Philippine Islands, has been examined by Clover (*Philippine J. Sci.*, 1906, **1**, 191), who found it to contain an unknown crystalline hydrocarbon and a mixture of sesquiterpenes from which a good yield of cadinene dihydrochloride was obtained.

We have now made a more complete examination of the oil, for a sample of which we are much indebted to Mr. Walter L. Brooke, Bureau of Science, Manila. The crystalline solid, which is present to the extent of a few units %, is triacontane, $C_{30}H_{62}$. From one of the fractions of the oil we have obtained a second *compound*, m. p. 172—178°; this appears to be another substance of high molecular weight, but the quantity of it so far available has not permitted a more complete examination of its properties.

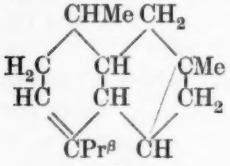
The volatile portion of the oil does not contain cadinene to any large extent, but the dihydrochloride which is obtained in good yield on treating certain fractions with hydrogen chloride is derived from a *tricyclic* sesquiterpene whose structure is evidently closely related to that of cadinene but whose physical properties differ considerably from those of pure regenerated cadinene. Deussen (*Arch. Pharm.*, 1900, **238**, 149; 1902, **240**, 288) has shown that the naturally occurring sesquiterpene in West Indian sandalwood oil which yields cadinene dihydrochloride differs in optical properties from the regenerated product. More important, however, is the work of Semmler and Stenzel (*Ber.*, 1914, **47**, 2558) on African copaiba, from which they isolated a new tricyclic sesquiterpene, copaene, which gave a 30% yield of cadinene dihydrochloride. The

principal fraction which we have obtained from supa oil is almost identical in its physical properties with Semmler's copaene and differs markedly from pure cadinene, as the following table shows:

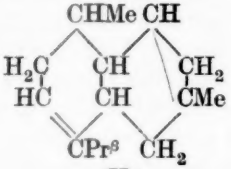
	B. p./ 10 mm.	$d_4^{15-20°}$.	$n_D^{15-20°}$.	$[R_L]_D$.	$[\alpha]_{5461}^{18°}$.
Principal fraction from supa oil	115—117°	0·9074	1·4944	65·4	−15·98°
Copaene	119—120	0·9077	1·4894	65·0	−13·35 (for D line)
Cadinene	130—134	0·9189	1·5097	66·4	−125

Supa oil therefore appears to offer a new and more convenient source of copaene than African copaiba, from which the separation of the copaene is complicated by the presence of other sesquiterpenes.

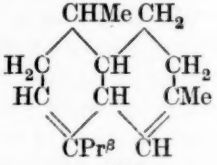
The relationship of copaene to cadinene was further established by Ruzicka's dehydrogenation method. When the former compound was heated with sulphur, complete dehydrogenation occurred, and a good yield of cadalene was isolated. In view of this result, and also since copaene is readily transformed into cadinene by the action of acids, it is evident that copaene contains the dicyclic cadinene structure (III), and that the third ring must take the form of an easily ruptured bridge, probably of the sabinene type. Hence Semmler's provisional formula for copaene (I) requires revision, and (II) more probably represents the structure of this sesquiterpene.



(I.)



(II.)



(III.)

EXPERIMENTAL.

Distillation of Supa Oil.—The oil consisted of a pale yellow, mobile liquid containing leaflets of a colourless solid, and possessed a faint but characteristic odour. After a number of fractional distillations under reduced pressure, the following fractions were isolated: (*a*) a colourless, mobile liquid, b. p. 115—117°/10 mm., constituting about 50% of the original sample; (*b*) a smaller fraction, b. p. 120—130°/10 mm., which after several distillations still boiled over a range of 10° and appeared to be a mixture; (*c*) a very small portion, b. p. 130—140°/10 mm. No distillate was obtained above 140°. The residue (*d*) when cold consisted of a brown, semi-solid mass which, however, was not resinous.

Conversion of the Copaene Fraction into Cadinene and Cadalene.—The fraction (*a*) after several distillations remained unaltered in

b. p. and had the physical properties recorded above ($[R_L]_D$ found, 65·4; calc. for a tricyclic sesquiterpene, 64·4; the large exaltation is consistent with the type of structure postulated by Semmler) (Found : C, 87·8; H, 11·6. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%).

A solution of the fraction (*a*) (20 g.) in glacial acetic acid (60 g.), when gradually treated at 0° with hydrogen chloride, became greenish-blue and finally red. After saturation the solution was kept for 24 hours at 0°; the crystals then formed, after purification, melted at 118°, alone or mixed with cadinene dihydrochloride (yield, 35% of fraction *a*).

For comparison of this yield with that obtained from other ethereal oils, an examination was made of samples of oil of cubebs and of maracaibo copaiba. The chief sesquiterpene fraction from oil of cubebs had b. p. 130—140°/10 mm. and consisted principally of cadinene, but a small fraction was obtained, b. p. 110—120°/10 mm. This on similar treatment with hydrogen chloride yielded only 2—4% of cadinene dihydrochloride. The lowest-boiling portion of maracaiba copaiba had properties somewhat similar to those of copaene, but upon treatment with hydrogen chloride a mixture of the dihydrochlorides of cadinene and caryophyllene was obtained.

The copaene fraction (*a*) (9 g.) was heated with sulphur (4·5 g.) at 200—250° for 1½ hours. Hydrogen sulphide was evolved freely at the latter temperature. The product was freed from sulphur by distillation over sodium under reduced pressure, and yielded an oil, b. p. 130—160°/12 mm., which was identified as cadalene by means of its picrate, m. p. and mixed m. p. 114—115°.

The Higher-boiling and the Solid Constituents of Supa Oil.—The fraction (*b*), b. p. 120—130°/10 mm., was a mixture. In a solution in a large excess of acetone, a fine, white precipitate formed, which became flocculent upon agitation; it could not be satisfactorily purified by crystallisation, but was obtained in a relatively pure condition as an amorphous, white powder by repeated dissolution in anhydrous ether and precipitation by an excess of acetone; m. p. 172—178° (Found : C, 86·9; H, 10·2%).

The residue (*d*) was dissolved in ether, and an excess of ethyl alcohol added. The white solid that separated was difficult to free from adhering oil by crystallisation from acetone, and more than ten crystallisations were necessary before the pure substance was obtained as fine flakes with a nacreous lustre, m. p. 63—64°. The compound is readily soluble in ether and in hot alcohol and acetone, but only very slightly soluble in benzene (Found : C, 84·8; H, 14·5; *M*, in camphor, 429, 420, 421, 443. $C_{30}H_{62}$ requires C, 85·3; H, 14·7%; *M*, 422).

After removal of the solid paraffin in the manner described, the viscous liquid residue gave, on vacuum distillation, a small quantity of a viscous, slightly yellow liquid, b. p. 145—155°/10 mm., $d_{4^\circ}^{15^\circ}$ 0·9484, in which the presence of a sesquiterpene alcohol is indicated (Found: C, 84·3; H, 11·5%).

We are indebted to the Carnegie Trust for a grant in aid of this work.

UNIVERSITY OF GLASGOW. [*Received, October 8th*, 1926.]

CCCCXIII.—*The Structure of the Benzene Nucleus. Part V. Some* meso*-Derivatives of Anthracene.*

By CHRISTOPHER KELK INGOLD and PHILIP GUY MARSHALL.

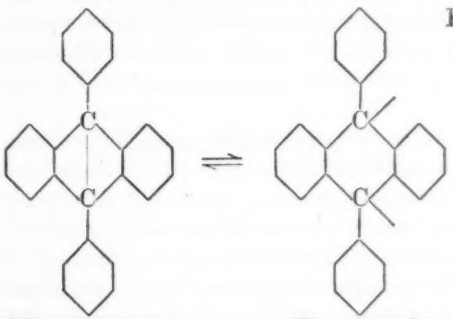
THE suggestion underlying the preceding parts of this series (J., 1922, **121**, 1133, 1143; 1923, **123**, 2066, 2081) that the propagation of reactivity from a substituent to the para-position of an aromatic ring occurs by direct affinity exchange in the Dewar form, regarded as one of the intra-annular phases to which the reactivity of the nucleus is due,* has been supplemented by numerous analogies with the *cyclo*pentadienes in which the evidence of trans-annular affinity exchange is particularly strong.

In the benzene series, however, it frequently happens that two views (neither necessarily excluding the other), namely, propagation round the ring in the Kekulé form, and by direct affinity exchange across it in the Dewar form, are equally applicable. Therefore, illustrated by any *op*-substitution of the ordinary type, the theory that the antecedent activation of the nucleus occurs by "Lewis displacement" in the intra-annular forms

is an obvious variant of the electronic strain-propagation scheme given by Ingold and Ingold (this vol., p. 1312, fig. C_1); whilst the corresponding view of *op*-deactivation (Holleman) during *m*-substitution (same formulæ with arrows reversed) avoids the difficulty encountered by a conjugation mechanism in explaining the practically exclusive *op*-substitution of such fully conjugated compounds as ω-nitrostyrene and cinnamic acid; it has also other advantages.

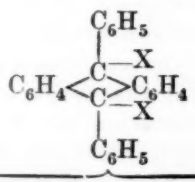
* The authors accept Bamberger's theory of the aromatic sextuple valency-group (*Ber.*, 1891, **24**, 1758; 1893, **26**, 1946; *Annalen*, 1893, **273**, 373) as representing the resting condition of the nucleus, but regard the sextuple association as peripheral (Thiele) rather than centric.

The problem of distinguishing between these two views is a difficult one and requires a separate solution for each group of aromatic phenomena. This paper records the results of an attempt to make the decision for the dissociation of the carbon–carbon bond, and the principle employed is as follows. The reactivity of the *meso*-carbon atoms of anthracene is well known and has recently been profusely illustrated (Barnett, Cook). The question to be answered is: Does this activity arise solely from the disturbance by the lateral rings of the equal distribution of valency *around* the central ring; or is it to be attributed to a phase in which there exists direct affinity exchange *across* the ring, that is, to a dissociable para-bond? According to the former alternative, the attachment of two phenyl nuclei to the 9- and 10-positions should, by conjugation, absorb this free affinity and 9 : 10-diphenylanthracene should exhibit less *meso*-reactivity than anthracene itself.* According to the latter view, however, the reverse *might* hold, since in this case there will be *one* phase in which the condition of the *meso*-carbon atoms is comparable with the condition of the ethane carbon atoms in a hexa-arylethane: each is joined to three benzene rings and to another carbon atom exactly like itself (III); and just as hexaphenylethane reversibly dissociates (V), so diphenylanthracene, and diarylanthracenes generally, should *internally* dissociate (IV), and should exhibit (doubtless in a subdued form, for this condition applies to only one of the intra-annular phases) those properties indicative of free affinity which are so strikingly displayed by the typical tervalent carbon radicals.



(III; colourless.) (IV; coloured.)

$$\underset{\text{(colourless)}}{Ph_3C{-}CPh_3} \rightleftharpoons \underset{\text{(coloured)}}{2CPh_3} \quad \text{(V.)}$$



VI, X = K, Na. VII, X = Cl, Br.
VIII, X = OH. IX, X = NHR.

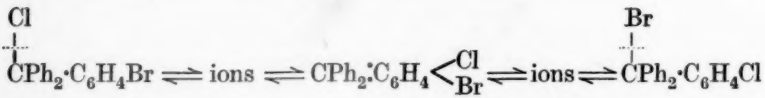
Actually, the 9 : 10-diarylanthracenes and substituted 9 : 10-diarylanthracenes which we have prepared exhibit characteristics corresponding to those of the hexa-arylethanes; *e.g.*, they are colourless or nearly so, in the solid state, but form coloured solutions (*e.g.*, in xylene) the colour of which (indicating dissociation) increases in

* Steric hindrance would work in the same way.

intensity with increase of temperature, and fades to its original depth on cooling; they form derivatives of type (VI) with the alkali metals in liquid ammonia, are readily oxidised and reduced in the 9- and 10-positions and add on halogens reversibly in these positions; the halogen compounds (Type VII), like triarylmethyl halides, are sensitive to water, giving carbinols (Type VIII), and to bases, giving amines of type (IX). All the reactions, however, except the rapid development of colour in solution, are noticeably less facile than the corresponding reactions of triphenylmethyl. Three points require elaboration :

(i) In electrolytically dissociating solvents the dissociation of triarylmethyls is, at least partly, ionic, and Gomberg's experiments have shown (compare Flürscheim, J., 1910, **97**, 92) that the positive triarylmethyl ion is tautomeric with its semi-quinonoid isomeride :

The proof of this is that *p*-bromotriphenylmethyl chloride and *p*-chlorotriphenylmethyl bromide, which are stable isomerides in non-ionising solvents, at once come into equilibrium when dissolved in an ionising solvent such as sulphur dioxide :



We have obtained evidence of an analogous condition of tautomerism both in the 9- and 10-phenyl rings, and in the lateral anthracene rings of our 9 : 10-diarylanthracene derivatives, using glacial acetic acid as the ionising solvent.

(ii) The tendency of the hexa-arylethanes and tetra-arylhydrazines towards dissociation into free radicals is known to be influenced by *p*-substituents, the effect of these in augmenting dissociation running roughly parallel with their *op*-directive power in aromatic substitution. To test this point for the diarylanthracenes, we have prepared a series of comparable *pp'*-disubstituted 9 : 10-diarylanthracenes, and, judging from the colour-intensities at equal molecular dilutions, we find for the order of the effect on dissociation : MeO > Me > Cl > H ; the effects due to Me and Cl are, however, very close together and the errors inherent in the method are such that their order cannot be guaranteed.

(iii) We have carried out a series of colorimetric measurements at different temperatures and concentrations in order to ascertain whether the relation between the colour depth, temperature, and

dilution corresponds with the requirements of a reversible unimolecular change of the type (III) $\rightleftharpoons$ (IV). The numerical results are consistent with this theory, although they are not sufficiently exact to establish it unequivocally, and the question whether the "degree of dissociation" should be taken in these cases to connote merely the proportion of fully dissociated isomeride, or whether mathematical recognition should be given to the continuous series of possible intermediate states (as in Debye's theory of electrolytic dissociation), is one which must await further evidence.

EXPERIMENTAL.

9 : 10-Dichloro- and 9 : 10-Dianilino-9 : 10-diphenyl-9 : 10-dihydroanthracene.—9 : 10-Dihydroxy-9 : 10-diphenyldihydroanthracene was prepared by Haller and Guyot's process (*Compt. rend.*, 1904, **138**, 327), modified with the object of improving the yield. The reaction product, which contained much unaltered anthraquinone, was decomposed with water, and the solid obtained was twice boiled with 500 c.c. of ethyl acetate. The combined, cooled, and filtered solutions, on concentration to a small bulk, deposited the dihydroxy-compound, which, after being washed with ligroin and crystallised from acetone, was obtained in 34% yield, m. p. 252—254° (Haller and Guyot record yield 10% and m. p. 242°).

A hot chloroform solution of the dihydroxy-compound, on saturation with hydrogen chloride, became turbid owing to separation of water; addition of acetic acid (2—3 vols.) then gave 9 : 10-dichloro-9 : 10-diphenyl-9 : 10-dihydroanthracene in colourless needles, m. p. 170° (decomp.), which were washed with acetic acid, water, and alcohol. This compound gave a deep yellow colour in liquid sulphur dioxide. When it was boiled with water, hydrochloric acid was gradually liberated and the dihydroxy-compound formed.

A solution of the dichloro-compound in hot benzene reacted very readily with aniline (4 mols.), aniline hydrochloride being precipitated (yield, 1·7 mols.; theoretical, 2·0 mols.). 9 : 10-*Dianilino*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene* crystallised when the filtrate was concentrated to a small bulk; it was washed with warm water to remove adhering aniline hydrochloride and recrystallised from benzene–ligroin, from which it separated in minute, colourless needles, m. p. 232—234° (Found: C, 88·8; H, 6·0. $C_{38}H_{30}N_2$ requires C, 88·7; H, 5·8%). It formed an orange solution in liquid sulphur dioxide and a blue solution in sulphuric acid.

9 : 10-Diphenylanthracene was obtained by treating the dihydroxy- or the dichloro-derivative with zinc dust and acetic acid, and from the latter by treatment with an aqueous solution of potassium iodide or carbamide. On chlorination in chloroform solution the dichloro-

derivative was re-formed, but the dibromo-derivative could not be produced in a similar way. An attempt to prepare the dibromo-compound by saturating an acetic acid solution of the dihydroxy-derivative with hydrogen bromide at 60° yielded only diphenyl-anthracene; from which it seems clear that the conversion of this substance into its 9 : 10-dihalogen addition products is reversible, and that whereas the dichloride is moderately stable, the dibromide and di-iodide lose their halogen with much greater ease (compare triarylmethyl halides). The hydrocarbon prepared by any of these methods separated from acetic acid or benzene in very pale yellow prisms, m. p. 249—250° (Found: C, 94·4; H, 5·4. Calc.: C, 94·5; H, 5·5%). It gave a deep yellow solution in liquid sulphur dioxide and yellow, fluorescent solutions in the ordinary organic solvents (p. 3089). It was stable in air at the ordinary temperature, but on heating was converted into a product which gave the colour reactions of the dihydroxy-compound; this could be obtained from the hydrocarbon by successive treatment with silver oxide in xylene and with water.

When sodium or potassium was added to a solution of 9 : 10-diphenylanthracene in anhydrous liquid ammonia, a bright cherry-red solution was formed which soon deposited a brick-red, amorphous precipitate. These precipitates apparently consisted of the 9 : 10-*disodio-* and 9 : 10-*dipotassio*-derivatives of 9 : 10-diphenyl-9 : 10-dihydroanthracene. They were less stable than the corresponding compounds prepared from triphenylmethyl (Kraus and Kawamura, *J. Amer. Chem. Soc.*, 1923, **45**, 2756), and were not purified owing to their instability in moist air. By taking advantage of the intense colour of the solutions of the alkali metals in ammonia, however, indirect analyses were carried out: a known weight of the hydrocarbon dissolved in liquid ammonia was titrated with a solution of potassium or sodium in the same solvent until one more drop gave a maroon or purple end-point; the ammonia was then evaporated and the residue was dried over sulphuric acid, decomposed with water, and titrated with standard hydrochloric acid* (Found: K, 19·8. Na, 13·8. $C_{26}H_{18}K_2$ requires K, 19·1%. $C_{26}H_{18}Na_2$ requires Na, 12·2%). When water was added during these estimations, a small amount of a gas (presumably hydrogen) was evolved; the residue contained 9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, colourless needles with a bluish-violet sheen, m. p. 222—225° after crystallisation from acetone (Found: C, 93·9; H, 6·2. $C_{26}H_{20}$ requires

* To correct for the water content of the ammonia, a small quantity of sodium or potassium was dissolved in ammonia, and the solution diluted from the main stock until the colour vanished. The volume was then noted, and the alkali hydroxide remaining after evaporation estimated.

C, 94·0; H, 6·0%), but also gave, before purification, the colour reactions of 9 : 10-diphenylanthracene.

9 : 10-*Dihydroxy*-9 : 10-*di*-p-*tolyl*-9 : 10-*dihydroanthracene*.—A suspension of anthraquinone (45·5 g.) in 300 c.c. of dry ether was gradually added to the Grignard solution prepared from *p*-iodotoluene (100 g.), magnesium (10·8 g.), ether (220 c.c.), and a trace of iodine. After the mixture had been boiled under reflux for 4 hours, the solid product was collected and decomposed with very dilute hydrochloric acid. The material thus obtained was twice extracted with 500 c.c. of boiling ethyl acetate, and the combined filtrates were concentrated and mixed with ligroin. The crystalline product was collected, washed with ligroin, and crystallised from toluene, from which colourless needles, m. p. 267—270°, separated. A further crystallisation from acetone, alcohol, or pyridine raised this m. p. to 275°, perceptible softening taking place at 270° (yield, 18%) (Found : C, 85·9; H, 6·2. $C_{28}H_{24}O_2$ requires C, 85·7; H, 6·2%). The compound gave a yellow solution in liquid sulphur dioxide and a deep blue solution in sulphuric acid.

9 : 10-*Di*-p-*tolylanthracene*.—Zinc dust was added at intervals during 1 hour to a boiling solution of the dihydroxy-compound (5 g.) in glacial acetic acid (50 c.c.). The solution (final volume, 30 c.c.) was well cooled and filtered, and the hydrocarbon extracted from the residue with boiling toluene. The product, obtained by concentrating the extract, was again crystallised from toluene; very pale yellow prisms were then obtained, m. p. 278—279° (Found : C, 93·7; H, 6·3. $C_{28}H_{22}$ requires C, 93·8; H, 6·2%). This substance closely resembles the diphenyl analogue (see, however, p. 3089). Yield 63%. The *dipotassio*- and *disodio*-derivatives were obtained as in the case of the diphenyl derivatives (Found : K, 18·9. Na, 10·7. $C_{28}H_{22}K_2$ requires K, 17·9%. $C_{28}H_{22}Na_2$ requires Na, 11·4%).

9 : 10-*Dihydroxy*-9 : 10-*di*-p-*chlorophenyl*-9 : 10-*dihydroanthracene*.—A suspension of anthraquinone (30 g.) in ether (250 c.c.) was added gradually to a Grignard solution prepared from *p*-chloroiodobenzene (95 g.), magnesium (9·5 g.), and 250 c.c. of ether; the product was isolated like the dihydroxyditolyl compound and obtained in colourless, prismatic needles, m. p. 267° (decomp.). It is similar in all respects to the ditolyl analogue (Found : C, 72·3; H, 4·3. $C_{26}H_{18}O_2Cl_2$ requires C, 72·1; H, 4·2%). This analysis and qualitative tests showed that the product contained no di-iodophenyl derivatives.

9 : 10-*Di*-p-*chlorophenylanthracene* was prepared in the same way as ditolylanthracene, except that xylene was used for the extraction and crystallisation of the product, m. p. 306—307·5° (Found : C, 78·3; H, 4·3. $C_{26}H_{16}Cl_2$ requires C, 78·2; H, 4·0%), which had

properties closely similar to those of the tolyl compound (compare, however, p. 3089). Yield, 60%.

In an unsuccessful attempt to synthesise 9 : 10-dibromo-9 : 10-di-*p*-chlorophenyl-9 : 10-dihydroanthracene, the above dichlorohydrocarbon was reduced to 9 : 10-*di*-p-*chlorophenyl*-9 : 10-*dihydroanthracene* by adding sodium amalgam to a boiling alcoholic suspension until the fluorescence had almost disappeared. The mercury was removed, the suspension mixed with water, and the solid material collected. A filtered solution of this in hot toluene, after admixture with absolute alcohol (2 vols.), gave colourless needles, m. p. about 206°. The filtrate from this, on being concentrated and mixed with a further quantity of alcohol, yielded colourless needles, m. p. about 165° (Found: C, 77·7; H, 4·7. $C_{26}H_{18}Cl_2$ requires C, 77·8; H, 4·5%). A mixture of *cis*- and *trans*-isomerides would be expected.

9 : 10-*Dihydroxy*-9 : 10-*di*-p-*bromophenyl*-9 : 10-*dihydroanthracene* was prepared in the usual way, 25 g. of anthraquinone suspended in 250 c.c. of ether, and a Grignard solution prepared from 90 g. of *p*-bromoiodobenzene, 7·56 g. of magnesium, and 200 c.c. of ether being used. The product separated from xylene or ethyl acetate–ligroin in colourless, prismatic needles, m. p. 273—274° (Found: C, 60·0; H, 3·4. $C_{26}H_{18}O_2Br_2$ requires C, 59·8; H, 3·4%). Its properties are similar to those of the chloro-compound.

9 : 10-*Di*-p-*bromophenylanthracene* was prepared in the same way as the chloro-analogue; it shrank at 315° and melted at 326—327° (Found: C, 63·9; H, 3·4. $C_{26}H_{16}Br_2$ requires C, 63·9; H, 3·3%).

9 : 10-*Dihydroxy*-9 : 10-*di*-p-*anisyl*-9 : 10-*dihydroanthracene* was obtained from 40 g. of anthraquinone, suspended in ether (250 c.c.), and a Grignard solution prepared from *p*-bromoanisole (93·5 g.), magnesium (12·0 g.), and ether (250 c.c.). After the product had been decomposed with dilute hydrochloric acid, the dianisyl compound was extracted by boiling the solid material three times with 400 c.c. of ethyl acetate. The concentrated extracts were allowed to cool and the crystalline product was freed from gummy impurities by washing with alcohol and from anthraquinone by filtering its solution in boiling acetone. A further crystallisation from acetone yielded colourless needles, m. p. 258—262° (yield, 31 g.). This compound gives a brilliant cherry-red solution in sulphuric acid (Found: C, 79·3; H, 5·7. $C_{28}H_{24}O_4$ requires C, 79·2; H, 5·7%).*

9 : 10-*Di*-p-*anisylanthracene*, prepared in the usual way and crystal-

* On heating with phosphorus and hydriodic acid at 150°, this substance yielded a hydrocarbon, m. p. 105—108°, forming colourless leaflets when crystallised from ligroin. Analysis (Found: C, 92·7; H, 7·5. $C_{26}H_{26}$ requires C, 92·3; H, 7·7%) indicated that it is *octahydro*-9 : 10-*diphenylanthracene*.

lised from toluene containing a little ligroin, was obtained in very pale yellow prisms, m. p. 282° (Found : C, 85·7; H, 5·7. $C_{28}H_{22}O_2$ requires C, 86·2; H, 5·9%). It gives an olive solution in sulphuric acid, and otherwise resembles its analogues (compare, however, p. 3089).

2-*Chloro*-9 : 10-*dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene* was prepared from 2-chloroanthraquinone (42·5 g., suspended in ether, 250 c.c.) and the Grignard derivative obtained from bromobenzene (60 g.), magnesium (8·72 g.), and ether (150 c.c.), and was crystallised from toluene–ligroin (4 : 1); m. p. 220—221° (Found : C, 78·7; H, 5·1. $C_{26}H_{19}O_2Cl$ requires C, 78·3; H, 4·8%). Its solution in concentrated sulphuric acid is indigo-blue.

2-*Chloro*-9 : 10-*diphenylanthracene*, prepared in the usual way by reduction of the dihydroxy-compound, and extracted from the zinc, etc., with ligroin, formed small, pale yellow crystals, m. p. 193°. It is much more soluble in the usual solvents than 9 : 10-diphenylanthracene, which it otherwise resembles (Found : C, 86·0; H, 5·0. $C_{26}H_{17}Cl$ requires C, 85·6; H, 4·7%).

2-*Bromo*-9 : 10-*dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*, prepared from 2-bromoanthraquinone (78 g., suspended in ether, 250 c.c.) and the Grignard compound from bromobenzene (120 g.), magnesium (17·4 g.), and ether (300 c.c.), separated from acetone in colourless needles, m. p. 206—209° (Found : C, 70·8; H, 4·3. $C_{26}H_{19}O_2Br$ requires C, 70·4; H, 4·3%). It resembles the 2-chloro-compound.

2-*Bromo*-9 : 10-*diphenylanthracene* was prepared in the same way as its chloro-analogue, except that acetone was used in place of ligroin for the extraction. Crystallised from acetone–ligroin, it formed very pale greenish-yellow needles, m. p. 185—187° (Found : C, 76·5; H, 4·3. $C_{26}H_{17}Br$ requires C, 76·3; H, 4·1%).

9-*Hydroxy*-9-*triphenylmethylanthrone* was obtained during some unsuccessful attempts to synthesise 9 : 10-bistriphenylmethylanthracene. The Grignard compound prepared from triphenylchloromethane (36 g.), magnesium (3·1 g.), and ether (100 c.c.) was treated with anthraquinone (11 g.) suspended in ether (80 c.c.); the product was worked up as usual. After several crystallisations from toluene, colourless prisms, m. p. 183—190°, were obtained (Found : C, 87·6; H, 5·7. $C_{33}H_{24}O_2$ requires C, 87·6; H, 5·3%). It gives a yellow solution in sulphuric acid.

Action of Hydrogen Chloride on 9 : 10-*Dihydroxy*-9 : 10-*di*-p-*bromophenyl*-9 : 10-*dihydroanthracene and of Chlorine on* 9 : 10-*Di*-p-*bromophenylanthracene* : *Formation of* 9 : 10-*Dichloro*-9 10-*di*-p-*bromophenyl*-9 : 10-*dihydroanthracene and* 9 : 10-*Di*-p-*chloroanthracene*.—The dihydroxy-compound (1 g.) dissolved in hot glacial acetic acid

was treated with a stream of hydrogen chloride for 5 minutes. After cooling, the crystals were collected, washed with acetic acid, and crystallised from benzene, almost colourless needles, m. p. 218°, being obtained. 9:10-*Dichloro*-9:10-*di*-p-*bromophenyl*-9:10-*dihydroanthracene* gives a deep blue colour with concentrated sulphuric acid and an orange-yellow solution in liquid sulphur dioxide (Found: C, 55·7; H, 3·0. $C_{26}H_{16}Cl_2Br_2$ requires C, 55·8; H, 2·9%). The same substance is formed when chlorine is passed into a solution of 9:10-di-*p*-bromophenylanthracene in chloroform. It does not appear to undergo rearrangement (except possibly to a small extent) in liquid sulphur dioxide: whether this is due to slow reaction at the low temperature or to an unfavourable equilibrium we have not been able to determine, since the 9:10-dibromo-9:10-di-*p*-chlorophenyl-9:10-dihydroanthracene required to investigate the reverse change could not be prepared (pp. 3084, 3086). Evidence of the occurrence of the rearrangement in hot glacial acetic acid was, however, obtained by the isolation of 9:10-di-*p*-chlorophenylanthracene from the product formed by treating the dihydroxydi-*p*-bromophenyl compound for ½ hour with hydrogen chloride in hot glacial acetic acid. In another experiment, the treatment with hydrogen chloride was continued for 15 minutes, and the solution boiled for 15 minutes. The product, crystallised repeatedly from toluene and then from toluene–alcohol, gave (*a*) a sparingly soluble product, m. p. 290—320°, containing chlorine and bromine, which was not further investigated, (*b*) di-*p*-chlorophenylanthracene (m. p. 304—306°; mixed m. p. 305—307°) (Found: C, 78·0; H, 4·3. Calc.: C, 78·2; H, 4·0%), (*c*) a product, m. p. 209—214° (mixed m. p. with 9:10-dichloro-9:10-di-*p*-bromophenyl-9:10-dihydroanthracene, 212—215°), containing both chlorine and bromine, which, however, could not be completely purified. Since 9:10-dibromo-9:10-di-*p*-chlorophenyl-9:10-dihydroanthracene would lose bromine spontaneously, giving 9:10-di-*p*-chlorophenylanthracene under the conditions employed, we regard these observations as establishing the series of reactions referred to on p. 3082.

Action of Hydrogen Chloride on 2-*Bromo*-9:10-*dihydroxy*-9:10-*diphenyl*-9:10-*dihydroanthracene.*—The bromodihydroxy-compound was treated in boiling glacial acetic acid solution with hydrogen chloride for 1·5 hours. After cooling, the yellow product was collected and separated into two portions by filtering its suspension in boiling acetone. The undissolved portion, after crystallising three times from toluene and twice from pyridine, formed very pale greenish-yellow needles, m. p. 294—295°, which contained chlorine but no bromine (Found: C, 73·3, 73·4; H, 3·8, 3·9; Cl, 23·8. $C_{26}H_{15}Cl_2$ requires C, 72·0; H, 3·5; Cl, 24·5%). This compound,

which was obviously of the 9 : 10-diarylanthracene type and gave with cold xylene a yellow solution which became intensely orange-yellow at the boiling point, appears to contain one atom of chlorine more than 2 : 3-dichloro- or 2 : 6-dichloro-9 : 10-diphenylanthracene, the highest-chlorinated bromine-free derivatives we expected to obtain, and there are many conceivable ways in which this result may have been brought about. The product soluble in acetone, after further crystallisation from acetone and toluene–ligroin, had m. p. about 175° and obviously consisted largely of 2-chloro-9 : 10-diphenylanthracene (mixed m. p. 187—192°), although it could not be entirely freed from a bromine-containing impurity. Since its reactions were exclusively those of a diarylanthracene, we conclude that the persistent impurity was probably 2-bromo-9 : 10-diphenylanthracene.

Colorimetric Determinations.—The following table records the length of the column of a colour-standard against which solutions of 9 : 10-di-*p*-anisylanthracene were matched at different temperatures. These solutions each contained 0·5 g. in 100 c.c.; the measurements refer to solutions in (*a*) mesitylene, (*b*) benzylidenemethylamine, and (*c*) bromonaphthalene. Series of readings were taken,* with rising temperatures, † with falling temperatures.

	†	†	†	*	†	*	†
Solvent	*a*	*b*	*a*	*a*	*b*	*a*	*c*
Temp.	20°	40°	50°	85°	93°	120°	120°
Length (mm.)	2·5	3·0	4·0	9·5	12·0	19·5	18·5
	*	*	*	*	*	*	*
Solvent	*b*	*a*	*b*	*c*	*b*	*c*	*c*
Temp.	135°	140°	150°	158°	172°	220°	265°
Length (mm.)	20·5	25·0	27·5	30·0	36·0	50·5	57·0

Solutions of diphenylanthracene, di-*p*-tolylanthracene, di-*p*-chlorophenylanthracene, and di-*p*-anisylanthracene in benzylidenemethylamine were compared with the same colour-standard at 150°, and the following relative colour intensities obtained: 1·0, 1·4, 1·5, 2·7, respectively.

An approximately decimolecular solution of trichlorodiphenylanthracene (see above) in xylene was matched against a colour-standard and then diluted. The following colour intensities refer to the temperature 25°, for the relative dilutions 1·0, 2·4, 5·1 and 8·1, respectively: 7·7, 7·4, 7·8 and 7·9.

Similar results were obtained at 100°, indicating that the intensity of colour is substantially independent of concentration.

We desire to record our thanks to the Royal Society for a grant which has defrayed a part of the cost of this investigation.

THE UNIVERSITY, LEEDS. [*Received, October 9th,* 1926.]

CCCCXIV.—*The Alleged Nitration of* S-*Methylthioguaiacol. A Criticism.*

By Alfred Pollard and Robert Robinson.

Holmes, Ingold, and Ingold (this vol., p. 1684) have described the mononitration of *S*-methylthioguaiacol by means of a mixture of nitric acid and acetic anhydride and state that the liquid product, $SMe{\cdot}C_6H_3(OMe){\cdot}NO_2$, may be oxidised by cold fuming nitric acid to a related sulphone, $C_8H_9O_5NS$, m. p. 144—145°. This substance was found to differ from the 3-, 4-, and 5- nitro-2-methoxyphenylmethylsulphones, which were synthesised for comparison, and was by exclusion regarded as 6-nitro-2-methoxyphenylmethylsulphone. The conclusion was drawn that the nitroxyl entered the *o*-position to the methylthiol group and the authors, far from expressing surprise at so remarkable a result, proceeded to develop a theory which accommodated it. This hypothesis, which we consider to be an unsound development of the theory of crotenoid systems, cannot be discussed here because we do not understand it. We especially fail to comprehend the meaning of the phrase " externally neutralised " on p. 1686 (*loc. cit.*).

In short, we were disposed to doubt the correctness of Holmes, Ingold, and Ingold's conclusion as to the *o*-substitution both on theoretical grounds and from analogies. The logical but dangerous method of exclusion of alternatives, relied upon by these authors, as mentioned above, was not supplemented either by the synthesis of the remaining possibility or by the close examination of the supposed 6-nitro-2-methoxyphenylmethylsulphone. Confirmatory evidence was all the more to be sought in view of the well-known fact that nitric acid is usually employed to oxidise a sulphide to a sulphoxide rather than to a sulphone.

We have had no difficulty in obtaining the substance, m. p. 144—145°, by following the instructions of Holmes, Ingold, and Ingold, but find that it is a sulphoxide in that it may be further oxidised by potassium permanganate to a sulphone. The latter was identified as 5-nitro-2-methoxyphenylmethylsulphone, m. p. 149—150° (Holmes, Ingold, and Ingold, *loc. cit.*). In the combined nitration and oxidation of *S*-methylthioguaiacol, therefore, the substituent enters chiefly the *p*-position to the methoxyl group.

It occurred to us that the explanation of the ultimate production of 5-nitro-2-methoxyphenylmethylsulphone might be that oxidation precedes nitration and that actually 2-methoxyphenyl methyl sulphoxide is the substance that is nitrated. If so, the position

taken up by the substituent would be the normal one *p*- to the methoxyl group. This view cannot be reconciled with the results of Holmes, Ingold, and Ingold on the mononitration of *S*-methylthioguaiacol, which are very positive and described in the most precise manner; consequently we did not at first entertain the possibility. Nevertheless, on repetition of the experiment we obtained 2-methoxyphenyl methyl sulphoxide instead of the nitro-*S*-methylthioguaiacol which Holmes, Ingold, and Ingold state to be the product.

The nitration of *S*-methylthioguaiacol has not yet been accomplished and further work is necessary in order to establish the order of the directive efficiencies of sulphur and oxygen atoms directly attached to the aromatic nucleus.

Experimental.

2-Methoxyphenyl Methyl Sulphoxide.—*S*-Methylthioguaiacol crystallises on standing and melts at about 19°. When it is treated as described by Holmes, Ingold, and Ingold (*loc. cit.*, p. 1687) under the heading *Mononitration*, the chief product is a yellow oil which crystallises after distillation (Found: C, 55·7;* H, 6·6. $C_8H_{10}O_2S$ requires C, 56·9; H, 5·9%). (For a pale yellow oil, prepared in this way but not found to crystallise, Holmes, Ingold, and Ingold gave C, 47·8; H, 4·4. $C_8H_9O_3NS$ requires C, 48·0; H, 4·5%.) On vigorous reduction with zinc dust and boiling dilute hydrochloric acid an oil, volatile in steam and having the odour of *S*-methylthioguaiacol, is produced. Oxidation with potassium permanganate gives a good yield of 2-methoxyphenylmethylsulphone, identified by comparison and by the m. p.† (91°) of a mixture with an authentic specimen. The sulphoxide is difficult to recrystallise, but separates from light petroleum in colourless prisms, m. p. 44° (Found: C, 56·6; H, 6·0%).

5-Nitro-2-methoxyphenyl methyl sulphoxide was prepared by the action of cold fuming nitric acid on *S*-methylthioguaiacol as described by Holmes, Ingold, and Ingold (*loc. cit.*) under the heading: *6-Nitro-2-methoxyphenylmethylsulphone*. We did not succeed in obtaining the 80% yield claimed by these authors, but the substance crystallised from methyl alcohol in very pale yellow needles, m. p. 144—145°, in agreement with their description (Found in air-dried

* By microanalysis; a combustion on the ordinary scale gave a lower result for the carbon content.

† Troeger and Budde (*J. pr. Chem.*, 1902, **66**, 130) describe this sulphone as crystals, m. p. 84°, from alcohol. We have obtained it in colourless laminæ, m. p. 91°, from benzene–light petroleum.

material: C, 44·8; H, 4·2. $C_8H_9O_4NS$ requires C, 44·6; H, 4·2%). Holmes, Ingold, and Ingold gave C, 41·2; H, 3·9. $C_8H_9O_5NS$ requires C, 41·5; H, 3·9%.

The sulphoxide (0·85 g.) was dissolved in hot water (40 c.c.), and aqueous potassium permanganate (30 c.c. of 2%) added. After a few minutes, the small excess of the latter was reduced by alcohol, and the manganese dioxide converted into dithionate. The colourless precipitate (0·75 g.) crystallised from alcohol in colourless leaflets, which melted at 149—150° and at the same temperature when mixed with an authentic specimen of 5-nitro-2-methoxyphenylmethylsulphone (Holmes, Ingold, and Ingold, *loc. cit.*, describe pale yellow needles, m. p. 149°).

5-*Nitro*-2-*hydroxyphenylmethylsulphone*, $NO_2 \cdot C_6H_3(OH) \cdot SO_2Me$.—The sulphoxide, m. p. 144—145°, and the sulphone, m. p. 149—150°, are each readily hydrolysed by boiling dilute aqueous sodium hydroxide, yielding bright yellow alkaline solutions from which colourless compounds are precipitated on acidification. The reaction, strongly suggestive of the hydrolysis of *p*-nitroanisole derivatives, confirms our view of the nature of these substances. 5-Nitro-2-hydroxyphenylmethylsulphone dissolves in hot water to a yellow solution, from which flat, transparent needles are deposited on cooling; these change in contact with the solvent into an opaque, prismatic form, m. p. 167° (Found in material dried at 100°: N, 6·4, 6·4; S, 14·5. $C_7H_7O_5NS$ requires N, 6·5; S, 14·7%). The substance is readily soluble in aqueous sodium carbonate to a lemon-yellow solution. On the addition of bromine water to an aqueous solution a bromo-derivative is rapidly formed and soon separates in colourless, slender needles, m. p. 173°. This derivative dissolves in hot water to a bright yellow solution and is probably 3-bromo-5-nitro-2-hydroxyphenylmethylsulphone.

3 : 5-*Dinitro*-2-*hydroxyphenylmethylsulphone*.—A solution of 5-nitro-2-hydroxyphenylmethylsulphone in nitric acid (*d* 1·42) was boiled and then poured into water. The solid was collected and crystallised from water; a small amount of picric acid was isolated from the original acid liquor after concentration and removal of a further quantity of dinitrohydroxyphenylmethylsulphone. The latter crystallises from water or alcohol in brittle, sulphur-yellow needles, m. p. 166° (Found in material dried at 100°: N, 10·6; S, 12·1. $C_7H_6O_6N_2S$ requires N, 10·7; S, 12·2%). This substance resembles picric acid in its properties, dyes silk yellow, and develops a brownish-red coloration with aqueous potassium cyanide on heating.

The carbon, hydrogen, and nitrogen determinations (micro-methods) recorded in this paper were made by Mr. A. Bennett.

We desire to thank the Department of Scientific and Industrial Research for a grant which enabled one of us to take part in the work.

THE UNIVERSITY, MANCHESTER. [*Received, October 21st*, 1926. *Revised, November 3rd*, 1926.]

CCCCXV.—*Action of Nitric Acid on* S-*Methylthioguaiacol. A Correction.*

By CHRISTOPHER KELK INGOLD and EDITH HILDA INGOLD.

IN the course of a systematic repetition, now nearly completed, of work described in certain previous communications from this laboratory, the following error has been detected. Holmes, Ingold, and Ingold (this vol., p. 1684) described a compound, m. p. 144—145°, which had been obtained as the main product of the action of excess of fuming nitric acid on *S*-methylthioguaiacol, and, owing (as it now appears) to the coincidence of an erroneous carbon and hydrogen determination,* regarded it as 6-nitro-2-methoxyphenylmethylsulphone (*ibid.*, p. 1687), the orientation being deduced from its non-identity with 5-, 4-, or 3-nitro-2-methoxyphenylmethylsulphone, all of which had been synthesised by methods which placed their constitutions beyond doubt. We find, however, that the substance having m. p. 144—145° is really *5-nitro-2-methoxyphenyl methyl sulphoxide* for the following reasons: (1) We have analysed it, with these results: Found: C, 44·9, 44·6, 44·7; H, 4·4, 4·2, 4·4. $C_8H_9O_4NS$ requires C, 44·6, H, 4·2%. (A nitromethoxyphenylmethylsulphone would require C, 41·6; H, 3·9%). (2) We have also oxidised it (0·40 g.) by boiling for 8 minutes with 6 c.c. of dilute sulphuric acid (1 : 3 by volume) and potassium dichromate (0·30 g., previously dissolved in about 2 c.c. of water), and have thus obtained a sulphone (Found: C, 41·6; H, 4·0%), m. p. 147—148° (yield 0·27 g. after crystallisation from methyl alcohol; yield 0·40 g. and m. p. about 140° before crystallisation), which does not depress the m. p. of 5-nitro-2-methoxyphenylmethylsulphone prepared either from 4-nitro-*o*-anisidine or from 2-methoxyphenylmethylsulphone (*loc. cit.*).

The first action of nitric acid on *S*-methylthioguaiacol may be to convert it into the sulphoxide; alternatively,† the nitration may

* This may possibly have been due to the escape of methane or ethane, an occurrence which we have experienced on several occasions recently with sulphur compounds containing the methoxyl and similar groups.

† Analyses which have been made of the crude product, b. p. 144—146°/2 mm. (*loc. cit.*), suggest both actions.

occur through the thionium nitrate, and the oxidation subsequently. In either case, it follows that the desired information regarding the relative directive powers of oxygen and sulphur probably cannot be obtained from the study of the nitration of *OS*-dialkyl derivatives of monothiopyrocatechol, and therefore we propose to examine the action of substituting agents on other sulphur derivatives. Also, the most extreme case hitherto recorded of the vicinal substitution of an *o*-disubstituted benzene containing two *op*-directing groups is furnished now, not by *S*-methylthioguaiacol, but by *o*-fluoroanisole (*ibid.*, pp. 1328, 1686).

THE UNIVERSITY, LEEDS. [*Received, October 25th*, 1926.]

CCCCXVI.—*The Constitution of the Disaccharides. Part XI. Maltose.*

By WALTER NORMAN HAWORTH and STANLEY PEAT.

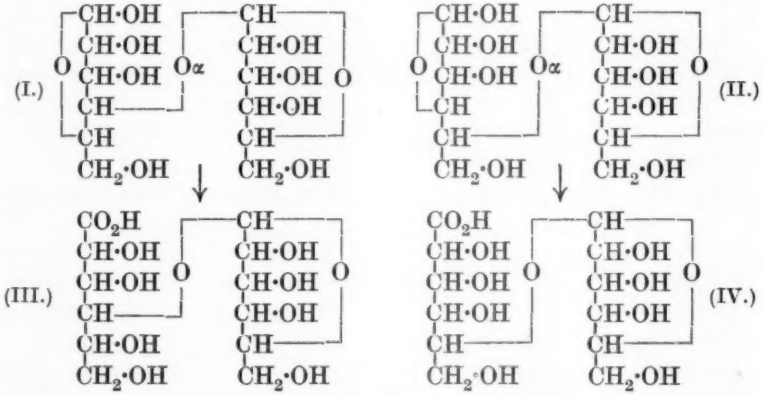
No conclusive proof of the constitution of maltose is available either from the research by Irvine and Black (this vol., p. 862) or from that by Cooper, Haworth, and Peat (*ibid.*, p. 876). In both papers, the evidence for the allocation of the two alternative formulæ (I) and (II) to maltose was based on the isolation of 2 : 3 : 6-trimethyl glucose obtained by the hydrolysis of completely methylated maltose.

As was pointed out by Charlton, Haworth, and Peat (this vol., footnote, p. 98), the isolation of 2 : 3 : 6-trimethyl glucose as a cleavage product of a methylated disaccharide does not enable a final decision to be reached as to the position occupied either by the original biose linking or by the oxide ring in the first hexose residue, since the alternative positions 4 and 5 are open for the allocation of either of these linkings. We therefore advanced, although guardedly, the suggestion that a butylene or γ-oxide (1 : 4) linking might be present in the first glucose residue in lactose and cellobiose, but we commented that this contingency was on the whole unlikely. In the later paper, we again left open this possibility in assigning a structural formula to maltose. The reason for this dubiety lay in our recognition of normal glucose as an amylene oxide and of γ-glucose derivatives as butylene oxides.

Prominence has been given by Irvine (this vol., pp. 868, 1495, 1507) to the tentative suggestion we made in the footnote above-mentioned, and in explicitly adopting this suggestion this author has asserted that in maltose and cellobiose different oxide rings occur in the first hexose residues. Thus, for maltose, Irvine and Black (this vol.,

p. 869) also proposed the two formulæ (I) and (II), adding the statement, "one of which must represent cellobiose and *iso*cellobiose, whilst the other must be reserved for maltose together with, presumably, *iso*maltose." This view has been further expanded and embodied by Irvine in the structural formulæ recently ascribed to starch (Irvine and Macdonald, this vol., p. 1508) and to cellulose (Irvine and Robertson, this vol., p. 1496). The constitutions allocated by these authors to the polysaccharides, although admittedly attractive, are based on an assertion which has, in view of the results now submitted, failed to receive experimental support. In view also of the inadequate knowledge available with regard to the constitution of *iso*maltose and *iso*cellobiose, it seemed to us to be premature at this stage to base a revision of the structural formulæ of the disaccharides and polysaccharides as a class upon the existence of these bioses.

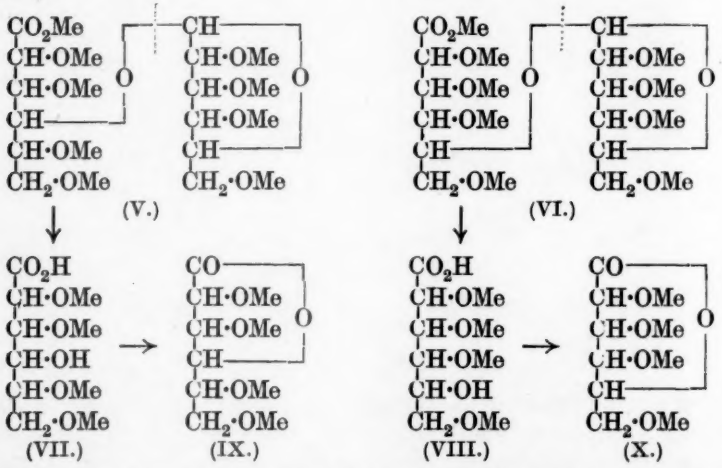
We have pursued the inquiry into the constitution of maltose and have instituted other experimental methods with the object of eliminating any dubiety in the case of this disaccharide.



The alternative formulæ (I) and (II) differ fundamentally in the position occupied by the biose linking. In formula (I) this linking engages the groups on the fourth carbon atom of the first glucose residue and the oxide ring is amylene oxidic; in formula (II) the biose linking is attached to the fifth carbon atom of the hexose chain, the oxide ring then being butylene oxidic. To reach a conclusive result it appeared to us essential that we should eliminate the oxide ring from the first hexose residue in maltose in order to concentrate attention on the position of the biose linking.

Maltose, on oxidation with bromine water, gives rise to maltobionic acid which, at the present stage of our knowledge, would be formulated either as (III) or (IV). It seemed possible to decide

between these alternatives by adopting the device of methylation, followed by hydrolysis to the constituent hexose acid and sugar. We therefore oxidised maltose to maltobionic acid and methylated the calcium salt of this acid with methyl sulphate and alkali, and thereafter the silver salt of the methylated acid was methylated by methyl iodide in presence of silver oxide. The compound so obtained was essentially methyl octamethylmaltobionate (V or VI), which distilled easily in a high vacuum. The hydrolysis of this ester with dilute mineral acid was accompanied by the cleavage of the bionic linking and resulted in the isolation of a tetramethyl gluconic acid (VII or VIII) along with crystalline tetramethyl glucose. On heating, the tetramethyl gluconic acid underwent ring closure, giving the corresponding tetramethyl gluconolactone (IX or X). The exposed hydroxyl group in (VII) or (VIII) represents the position of attachment of the original biose linking to the first hexose chain in maltose, and it is seen that the solution of the problem rests upon the diagnosis of the tetramethyl gluconolactone obtained and its recognition as belonging to the γ- or δ-series (IX or X).



We were in a position to decide this problem, since our earlier work had shown that the γ- and δ-lactones of glucose differ widely in their rates of hydrolysis, as revealed by polarimetric changes and by titration during hydrolysis. The crystalline tetramethyl lactone isolated from the above experiments corresponded in these respects with 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone, m. p. 26—27° (IX). Confirmation of this result was again possible in that the crystalline phenylhydrazide of 2 : 3 : 5 : 6-tetramethyl gluconic acid (VII) has a m. p. 134—136°, whilst the phenylhydrazide of 2 : 3 : 4 : 6-tetramethyl

gluconic acid (VIII) has a m. p. 114—115°. When the tetramethyl gluconolactone isolated as described above from methylated maltobionic ester was transformed into the phenylhydrazide, this had a m. p. 134—136°, and was identical in all respects with an authentic specimen derived from 2 : 3 : 5 : 6-tetramethyl gluconic acid. A mixed melting-point determination was made with the phenylhydrazides prepared from (*a*) the above lactone from methylated maltobionic acid, (*b*) the lactone obtained by oxidation, followed by methylation, of 2 : 3 : 6-trimethyl glucose, which we have shown to be a γ-lactone (this vol., p. 89), and (*c*) the lactone obtained by oxidation of tetramethyl γ-glucose, and in each case no depression of melting point occurred. The data for the recognition of the tetramethyl gluconolactone as a γ-lactone are based on these comparisons and are supplemented by the following facts.

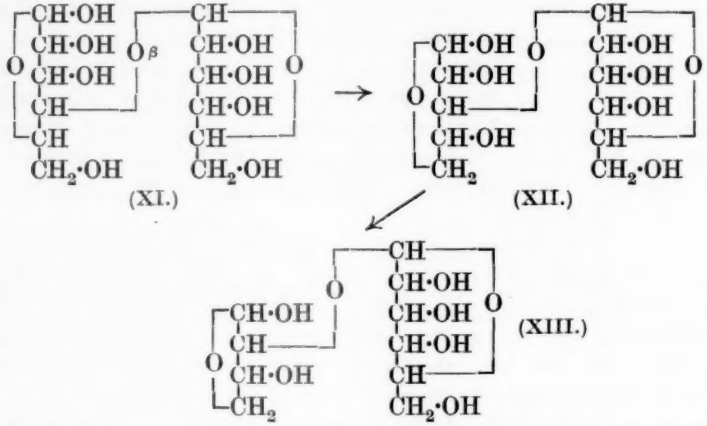
When crystalline tetramethyl glucose is oxidised to the corresponding lactone, this is identified as 2 : 3 : 4 : 6-tetramethyl δ-gluconolactone (X) (Charlton, Haworth, and Peat), and confirmation of this result has been contributed by Hirst (this vol., p. 389), who has also shown by other oxidation methods that crystalline tetramethyl glucose is substituted in positions 2, 3, 4, 6. The m. p., 114—115°, of the crystalline phenylhydrazide derived from this δ-lactone was depressed to 104—108° in a mixture with the present specimen.

Formulæ (V) and (VI) show that the maltobionic acid having the constitution (III) could alone give rise on complete methylation and hydrolysis to the γ-lactone. On the other hand, a maltobionic acid of the structure (IV), giving a methylated maltobionic acid of formula (VI), would lead to a δ-lactone (X) identical with that obtained on oxidising crystalline tetramethyl glucose, but this was found not to be the case.

The experimental data thus point to the allocation of formula (III) to maltobionic acid, and it therefore follows that, assuming no displacement of the biose linking either during methylation or during oxidation of maltose to maltobionic acid, the constitution of maltose should be represented by formula (I). We are at present engaged in applying the same method of proof to both lactose and cellobiose, and this work we wish to reserve.

Meanwhile, the constitution ascribed to cellobiose (Charlton, Haworth, and Peat, *loc. cit.*; Haworth and Hirst, J., 1921, **119**, 193) has received support from the work of Zemplén (*Ber.*, 1926, **59**, 1254), who has degraded cellobiose (XI) first to the hexose–pentose (XII), which gives an osazone, and finally to a hexose–tetrose (XIII), and the failure of the latter to form an osazone is attributed by this author to the presence of the biose linking on the carbon

atom adjoining the reducing group, *i.e.*, in position 4 in the original cellobiose. If this experimental work by Zemplén be accepted as a proof of the constitution of cellobiose, then it follows, from the evidence given in the present paper, that maltose and cellobiose possess the same constitution, the two disaccharides differing only in a stereochemical sense.



(XI.) (XII.) (XIII.)

A similar constitutional study of lactose by the same author (Zemplén, *Ber.*, 1926, **59**, 2402) confirms the structural formula we have applied to this disaccharide (Charlton, Haworth, and Peat, *loc. cit.*; Haworth and Leitch, 1918, **113**, 188).

The available evidence is thus opposed to the opinions expressed by Irvine (this vol., pp. 869, 1496, 1508) in his endeavour to classify the disaccharides and polysaccharides (starch and cellulose) on the basis of a difference in the positions of (*a*) the biose linking in maltose and cellobiose and (*b*) the oxide-ring linking in each of these bioses.

Experimental.

Methylation of Maltobionic Acid. Formation of Methyl Octamethylmaltobionate.—Pure maltose was oxidised with bromine water (Fischer and Meyer, *Ber.*, 1889, **22**, 1941; Glattfeld and Hanke, *J. Amer. Chem. Soc.*, 1918, **40**, 989), and the product isolated as calcium maltobionate. This was purified by solution in water and precipitation with alcohol, the process being repeated many times until reducing sugars were removed.

The calcium maltobionate was methylated several times in aqueous solution with methyl sulphate and alkali, the standard methods employed by one of us being adopted together with the modifications described in the researches on amygdalin (Haworth and Leitch, J., 1922, **121**, 1925; Campbell and Haworth, *ibid.*, 1924,

125, 1340). After methylation by methyl sulphate, the acid product was isolated from its salt and submitted again to a similar methylation procedure. The partly methylated maltobionic acid (Found: OMe, 41·7%) was now soluble in methyl iodide and was further methylated three times by Purdie's method.

It was essential throughout this investigation to ensure that any material which might have undergone hydrolysis during any stage of the manipulation should be completely eliminated (in order to avoid the presence of methylated gluconolactone or gluconic ester) from the product which was carried on to the final stages. The material (15 g.) was therefore fractionated at 0·03 mm. as follows, and the first fraction discarded:

Fraction	I.	B. p. → 155°.	Weight 2·0 g.	n_D 1·4470.
,,	II.	,, 160—165°.	,, 2·7 g.	,, 1·4610.
,,	III.	,, 167—170°.	,, 10·0 g.	,, 1·4638.

The last two fractions (Found: OMe, 52·7%) were united and twice re-methylated with moist silver oxide and methyl iodide and again with the dry Purdie reagents. The product (11 g.) appeared to contain heptamethyl maltobionolactone as well as the expected methyl octamethylmaltobionate, and failure to methylate it completely was attributed to the persistence of the lactone ring in the former of these constituents.

The whole of the material was dissolved in aqueous barium hydroxide at 40° and kept over-night. Thereafter the excess of barium hydroxide was removed by admitting carbon dioxide until the solution was neutral. The filtrate was analysed to determine its barium content, and then mixed with the equivalent proportion of aqueous silver sulphate for the precipitation of the barium as sulphate, this and the subsequent operations being conducted in a dark room. The filtered solution was completely evaporated at 35—40° under diminished pressure, and the residual silver salt, dried with methyl alcohol, was treated with a large excess of methyl iodide under reflux, the initial vigour of the reaction being moderated by cooling. Dry silver oxide and methyl iodide were afterwards added and the mixture was digested at 45°; the product ($n_D^{20°}$ 1·4603) was again distilled at 0·05 mm.

Fraction	Ia.	B. p. → 166°.	Weight 0·6 g.	$n_D^{17°}$ 1·4596.
,,	IIa.	,, 170—173°.	,, 8·7 g.	,, 1·4609.

The latter fraction (Found: OMe, 55·1%) was again submitted to three methylations, without any apparent change in boiling point or methoxyl content resulting, the final analytical figures being C, 51·5; H, 8·4; OMe, 55·4 (methyl octamethylmaltobionate, $C_{21}H_{40}O_{12}$, requires C, 52·1; H, 8·3; OMe, 57·8%). The compound was a pale yellow, viscid liquid, having $n_D^{14°}$ 1·4620.

The slightly low carbon value appeared to be due to analytical difficulties in the combustion, since by mixing the compound intimately with fine copper oxide in the combustion tube and repeating the analysis, the values C, 52·15; H, 8·3% were obtained.

Hydrolysis.—The above methyl octamethylmaltobionate was hydrolysed by heating at 80—90° with 7% hydrochloric acid ($c = 4·2$), and showed the following polarimetric changes: $[\alpha]_D$ + 120·8° (initial); 110·8° (after ½ hour); 88·1° (1½ hours); 70·5° (2·75 hours); 62·4° (3·75 hours); 57·5° (5 hours); 55·9° (6 hours); 54·9° (7 hours, remained constant). Heating for ¼ hour at 100° resulted in no further change, and there was little alteration in the colour of the solution during hydrolysis.

Isolation of Hydrolytic Products.—The acids, both inorganic and organic, present in the hydrolysed product were converted into the barium salts, and water was removed from the neutralised solution at 30°. The residue, dried with alcohol, was digested with boiling ether, which removed crystalline tetramethyl glucose, this being definitely characterised by the usual procedure (yield, quantitative). The saline residue was titrated with dilute hydrochloric acid to liberate the organic acid from its barium salt, and after this solution had been evaporated at 30°/15 mm. the residual mixture of barium chloride and organic acid was dried by heating at 60° in a vacuum. Ether extraction removed the organic portion, which was now chiefly a lactone (yield, 70% of the theoretical), and a further extraction of the barium residues with chloroform gave a further yield of the undecomposed barium salt (about 20%) of the acid corresponding to the above lactone.

Following a preliminary heating at 100° for ½ hour, the distillation of the lactone gave a colourless, mobile liquid, boiling constantly at a bath temperature of 110—115°/0·02 mm. (b. p. about 90°) and showing $n_D^{13°}$ 1·4490 and $n_D^{20°}$ 1·4470, which crystallised completely (m. p. 26—27°).

The weight of pure distilled material showing the above constants represented 85% of the total crude lactone, to which was added later the portion (approximately 10%) from the above-mentioned residual barium salt.

The lactone showed the following polarimetric changes in water ($c = 2$): $[\alpha]_D^{15°}$ + 60·2° (after ¼ hour); 57·3° (2 days); 55·2° (3 days); 54·2° (4 days); 51·2° (6 days); 43·1° (13 days) (Found: C, 51·0; H, 7·7; OMe, 52·3. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7; OMe, 53·0%).

Phenylhydrazide of 2 : 3 : 5 : 6-Tetramethyl Gluconic Acid.—The above lactone was mixed with the equivalent weight of phenylhydrazine in ether, the ether evaporated, and the residue heated at

100° for 5 minutes; it then solidified completely to a hard cake of colourless crystals. These were washed with ether, weighed (yield, quantitative), and purified from ether: m. p. 134—136° and re-melted at 135° after solidifying (Found: C, 55·8; H, 7·7; N, 8·2; OMe, 35·0. Calc.: C, 56·1; H, 7·6; N, 8·2; OMe, 36·3%).

The crystals of the phenylhydrazide were identified by m. p. determinations in admixture with each of the specimens of tetramethyl γ-gluconolactone prepared from (*a*) tetramethyl γ-glucose by oxidation with bromine water; (*b*) 2 : 3 : 6-trimethyl glucose by oxidation to 2 : 3 : 6-trimethyl γ-gluconolactone, which on methylation gave the 2 : 3 : 5 : 6-tetramethyl lactone (Charlton, Haworth, and Peat, this vol., p. 100). In each case there was no depression. For the purposes of this comparison the specimens prepared by the above authors were recrystallised several times (m. p. 134—136°). Among the residual portions of acid or lactonic products a search was made for the presence of a lactone which might give the phenylhydrazide of 2 : 3 : 4 : 6-tetramethyl gluconic acid (m. p. 114—115°), but no trace of this was discovered. A minute quantity of what appeared to be a trimethyl gluconolactone was, however, detected. There appeared to be no possibility of the presence of any tetramethyl lactone other than that described as 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone.

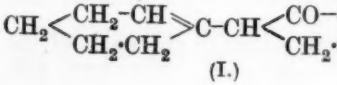
The authors are indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of them.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, October 26th,* 1926.]

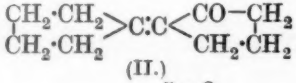
CCCCXVII.—*The Chemistry of the Three-carbon System. Part X. The Mobility of Some Cyclic Ketones.*

By GEORGE ARMAND ROBERT KON and JOHN HENRY NUTLAND.

IN our studies on compounds containing a potentially mobile three-carbon system we have investigated a group of ketones analogous to *cyclo*hexenylacetone (Part I, J., 1923, **123**, 1363) in which the ketone group forms part of a ring of five or six carbon atoms. The compounds examined include *cyclo*hexenyl*cyclo*hexanone (I), *cyclo*pentylidene*cyclo*pentanone (II), *iso*propylidene-*cyclo*pentanone (III), camphorphorone (IV), pulegone (V), and *iso*pulegone (VI).



(I.)



(II.)

(III.) $CMe_2{:}C\langle\begin{matrix}CO-CH_2\\CH_2{\cdot}CH_2\end{matrix}$ $\qquad$ $CMe_2{:}C\langle\begin{matrix}CO-CHMe\\CH_2{\cdot}CH_2\end{matrix}$ (IV.)

$CMe_2{:}C\langle\begin{matrix}CO-CH_2\\CH_2{\cdot}CH_2\end{matrix}\rangle CHMe$ $\qquad$ $CH_2{:}CMe{\cdot}CH\langle\begin{matrix}CO-CH_2\\CH_2{\cdot}CH_2\end{matrix}\rangle CHMe$

(V.) $\qquad$ (VI.)

From theoretical considerations, it was to be expected that the chemistry of these compounds would not differ fundamentally from that of the corresponding methyl ketones. This is so; *e.g.*, all the ketones can react in the αβ-form because they condense with ethyl sodiocyanoacetate; on the other hand, they can be alkylated on the α-carbon atom through their sodio-derivatives, which are necessarily derived from the βγ-phase.

There are, however, several points of interest in their chemistry. The first is the characteristic difference in the point of equilibrium of the compounds (I) and (II). The former has ordinarily the βγ-structure as shown by its normal molecular refraction and its behaviour on oxidation (compare Wallach, *Annalen*, 1911, **381**, 95), whereas the latter is stable in the αβ-form—it shows an exaltation of the molecular refraction and gives *cyclo*pentanone on oxidation. The difference is undoubtedly connected with the greater tendency of the six-membered ring to acquire a double bond, which stabilises the βγ-form. A similar difference has already been recorded in another series (Kon and Speight, this vol., 2727).

Another important feature is the ready conversion of the compounds (III) and (IV) into alkyl derivatives, the double bond moving into the βγ-position with the production of the group $CH_2{:}CMe{\cdot}CR<$. Up to the present, great difficulty had been experienced in obtaining βγ-derivatives from potentially mobile compounds in which the γ-carbon atom was not substituted, such as mesityl oxide (Kon, this vol., p. 1574) and dimethylacrylic acid (Kon and Linstead, J., 1925, **127**, 616). All the alkylated ketones have a lower density than the parent ketones (compare also Farrow and Kon, this vol., p. 2128).

The most interesting observation relates to pulegone and *iso*pulegone. Like the ketones (III) and (IV), both are readily methylated giving the same ketone (VII), which is a derivative of *iso*pulegone:

$$CH_2{:}CMe{\cdot}CMe\langle\begin{matrix}CO-CH_2\\CH_2{\cdot}CH_2\end{matrix}\rangle CHMe \quad \text{(VII.)}$$

$$CH_2{:}CMe{\cdot}CH\langle\begin{matrix}C(OH){:}CH\\CH_2-CH_2\end{matrix}\rangle CHMe \quad \text{(VIII.)}$$

The sodio-derivative is not derived from either of the enols of the type (VIII) prepared by Grignard (*Compt. rend.*, 1926, **182**, 422)

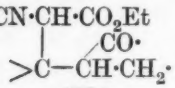
from both pulegone and *iso*pulegone; otherwise the methyl group would enter the position 6 and two *different* ketones would be produced.

This conclusion is supported by the observation that the dextrorotatory pulegone and the dextro- or lævo-rotatory *iso*pulegone (according as the natural or the synthetic ketone is employed) give the same strongly lævorotatory methyl or ethyl derivative. The latter is formed from a sodio-derivative common to both ketones and containing only *one* asymmetric carbon atom. The varying optical activity of *iso*pulegone is presumably due to the second asymmetric carbon atom which it contains. On the other hand, both pulegone and *iso*pulegone condense with ethyl cyanoacetate with equal readiness to give the same condensation product, so that these ketones are analogous to the two ketones described by Kon and Linstead (J., 1925, **127**, 815) in exhibiting retarded mobility; that is, whilst they are quite distinct and give rise to distinct derivatives, they become interconvertible in the presence of a reagent such as sodium ethoxide. The observation is of even greater interest when it is remembered that both pulegone and *iso*pulegone occur in nature. Indeed, there can be little doubt that tautomerism of the three-carbon or ring-chain type accounts for many of the changes observed in the terpene group.

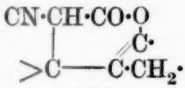
The semicarbazones of the compounds (I) and (II), like those of *cyclo*pentenyl- and *cyclo*hexenyl-acetone, occur in two forms; they probably differ in the position of the double bond, *i.e.*, represent the two individuals composing the liquid equilibrium mixture of ketones. The amount of the second form is generally small except in the case of *cyclo*pentenylacetone (Kon, J., 1921, **119**, 810). In this ketone the αβ-form should be favoured for the reason given on p. 3102 and the liquid equilibrium mixture should contain an appreciable quantity of it. This would account, not only for the comparable quantities of the two semicarbazones obtained, but also for the unusually high molecular refraction observed. The ketones regenerated from the pure semicarbazones (which, being crystalline solids, must have definite structures) again give a mixture on recombining with semicarbazide. Ketones such as camphorphorone, which give only one semicarbazone, may consist of one form only, like Kon and Linstead's ketones and pulegone and *iso*pulegone; or the equilibrium may be very much on one side.

The condensation of three compounds of this series with ethyl sodiocyanoacetate is abnormal: Vorländer (*Annalen*, 1906, **345**, 158) found that pulegone gave an unsaturated cyano-lactone (X), formed by loss of alcohol from the expected cyano-ester (IX);

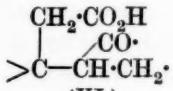
the same substance has now been obtained in equally good yield from *iso*pulegone, and with the ketone (I) an analogous reaction takes place. It is remarkable that the cyano-esters of type (IX) derived from the other ketones (all belonging to the *cyclo*pentane series) do not undergo internal ring formation and can be readily converted into the corresponding acetic acids (XI) on alkaline hydrolysis. The reason for this difference must be sought in the spatial effect of the *cyclo*hexane ring.



(IX.)



(X.)



(XI.)

Experimental.

2-Δ^1-cyclo*Hexenyl*cyclo*hexanone* (I).

The ketone was prepared in 80% yield as described by Wallach (*Ber.*, 1907, **40**, 70) and was purified by steam distillation before the final distillation under reduced pressure.

Semicarbazone. The recorded m. p.'s differ considerably; indeed, Brown and Ritter (*Ber.*, 1922, **55**, 3798), who isolated a semicarbazone, m. p. 191°, considered that their ketone was an isomeride of Wallach's, the semicarbazone of which melted at 179—181°. We have found that preparations of varying melting point were obtained owing to the presence, although in small amount, of a second form of the semicarbazone. The crude semicarbazone was prepared by adding 24 g. of the ketone in 200 c.c. of alcohol to a hot solution of 22 g. of semicarbazide hydrochloride and 35 g. of sodium acetate in 50 c.c. of water; the solid was collected after 12 hours, and a further quantity obtained by adding water to the mother-liquor. The dried solid was ground with light petroleum and extracted with boiling benzene. The residue, m. p. about 194°, was sparingly soluble in ethyl or methyl alcohol, benzene, acetone, or ethyl acetate and was best crystallised from the first or the last, being thus obtained in sparkling plates of constant m. p. 200—201° (Found: C, 66·7; H, 8·8. Calc. for $C_{13}H_{21}ON_3$: C, 66·4; H, 8·9%).

The benzene extract, on cooling, deposited a solid from which a certain amount of the semicarbazone, m. p. 200—201°, could be isolated; in addition, it contained a more soluble compound (about 2% of the total semicarbazone isolated) which crystallised from benzene and had m. p. 172° (Found: C, 66·5; H, 9·0%).

The ketone regenerated from the pure, high-melting semicarbazone by means of oxalic acid (this was used throughout this work) had b. p. 145°/17 mm., $d_4^{15\cdot1°}$ 1·00404, $n_D^{15\cdot1°}$ 1·50692, $[R_L]_D$ 52·81

(calc., 52·92). On reconverting it into the semicarbazone a mixture of the two forms, m. p. 200—201° and 172°, was once more obtained which could be separated as described above.

Oxidation. The pure ketone dissolved in dry chloroform was treated with ozone until absorption ceased. The ozonide was freed from chloroform under reduced pressure and boiled with water; on distillation in steam no volatile products were obtained. From the product, ether extracted adipic acid, which melted at 151° after two crystallisations from hydrochloric acid (yield, 3 g. from 5 g. of ketone). A better yield (4·5 g.) was obtained by conducting the ozonisation in the presence of water; no other products were isolated, although a special search was made for *cyclo*hexanone which could have resulted from the oxidation of the αβ-form of the ketone.

Methylation. The ketone was treated with methyl iodide and "molecular" sodium in ether (Kon, this vol., p. 1572). The ketone isolated boiled in part somewhat higher (146—152°/15 mm.) than the original ketone. The higher fraction was converted into the *semicarbazone*, which was ground with petroleum and thrice crystallised from alcohol; it then melted constantly at 204° and depressed the m. p. of the semicarbazone of the parent ketone (Found: C, 67·3; H, 9·4; N, 16·6. $C_{14}H_{23}ON_3$ requires C, 67·4; H, 9·3; N, 16·8%). The yield was about 15%.

2-*Methyl*-2-Δ^1-cyclo*hexenyl*cyclo*hexanone* regenerated from the semicarbazone had b. p. 150°/18 mm., $d_4^{19\cdot4°}$ 0·98804, $n_D^{19\cdot4°}$ 1·50320, $[R_L]_D$ 57·51 (calc., 57·52). Its constitution was confirmed by oxidation with ozone. The ozonide was warmed with water for an hour and the oily product was isolated by means of ether and treated with semicarbazide. After 12 hours, the semicarbazone was collected and recrystallised twice from alcohol; it had m. p. 145—146° and was evidently derived from δ-acetylvaleric acid (Found: C, 47·7; H, 7·4. Calc.: C, 47·8; H, 7·5%). The filtrate from this semicarbazone contained adipic acid.

Ethylation. Attempts to ethylate *cyclo*hexenyl*cyclo*hexanone under various conditions failed.

Condensation with ethyl sodiocyanoacetate. No condensation product could be obtained with ethyl sodiomalonate, and only a very small quantity of the nitrile (see below) with ethyl sodiocyanoacetate in alcoholic solution. The ketone (18 g.) was then heated for 24 hours with ethyl sodiocyanoacetate (1/10 mol.) prepared from "molecular" sodium in 100 c.c. of benzene. The cold mixture was poured into water and extracted with ether. The extract was distilled, 10 g. of the original ketone and 2 g. of a fraction, b. p. 200—260°(decomp.)/60—70 mm., being obtained; this frac-

tion solidified on cooling. A further 4 g. of the same substance were obtained on acidifying the aqueous solution obtained above and allowing it to stand for some time. The solid (27% yield) crystallised from alcohol or from benzene–petroleum in cubes, m. p. 112°, and was the *cyanolactone* of type (X) (Found : C, 73·7; H, 8·1; N, 5·9. $C_{15}H_{19}O_2N$ requires C, 73·4; H, 7·8; N, 5·7%). The same yield of the cyanolactone was obtained from the ketone recovered from a previous condensation and from the ketone regenerated from the pure semicarbazone. The compound resembles Vorländer's pulegone derivative (*q.v.*) in every respect. It dissolves in alkalis on warming and the solution rapidly becomes cloudy with the regeneration of *cyclo*hexenyl*cyclo*hexanone.

It was recovered unchanged after boiling for 2—3 hours with 60% sulphuric acid. A solution of it in excess of the concentrated acid was warmed to about 50°, left for 3 days, and poured into ice-water. The precipitate was collected, dried, and recrystallised alternately from benzene and dilute alcohol, being finally obtained in long needles, m. p. 166°; the compound was nitrogenous and appeared to be an *imide* (Found : C, 67·4; H, 9·5; N, 6·3. $C_{14}H_{21}ON$ requires C, 67·7; H, 9·7; N, 6·4%).

2-cyclo*Pentylidene*cyclo*pentanone* (II).

The ketone can be prepared in about 30% yield by either of the methods used by Wallach (*Ber.*, 1896, **29**, 2963); a 38% yield is obtained by using sodium ethoxide freed from alcohol under reduced pressure.

Semicarbazone. This compound was prepared and separated into two forms exactly as described on p. 3104. The less soluble form, after repeated crystallisation from ethyl and methyl alcohol, benzene, acetone, and ethyl acetate, formed plates, m. p. 223°, but darkening below this temperature (Found : C, 63·5; H, 8·2. $C_{11}H_{17}ON_3$ requires C, 63·8; H, 8·2%). The more soluble form had m. p. 207° (Found : C, 63·7; H, 8·2%). The proportion of the higher- and the lower-melting form isolated was about 20 : 1.

The ketone regenerated from the pure, high-melting form had b. p. 135°/25 mm., $d_4^{18·9°}$ 1·01787, $n_D^{18·9°}$ 1·52145, $[R_L]_D$ 44·95, in good agreement with Wallach's figures. The pure ketone gave a mixture of the same two semicarbazones, in the proportion of 20 : 1, when treated with semicarbazide.

Oxidation. This was carried out by means of ozone as before. The steam distillate contained a considerable quantity of *cyclo*pentanone, which was isolated by means of ether and identified in the form of its semicarbazone. The residue from the steam distillation contained glutaric acid, m. p. 97°, which was identified by

direct comparison with a genuine specimen. These two products establish the αβ-formula of the ketone.

Ethylation. Attempts to ethylate the ketone in the presence of sodium ethoxide were unsuccessful, but the reaction proceeded well with " molecular " sodium. The sodio-derivative was usually prepared in ethereal solution so as to avoid polymerisation; the ether was then distilled off and replaced by benzene before the addition of ethyl iodide. A considerable amount of the ketone isolated boiled at 140—150°/25 mm. The *semicarbazone* prepared from this fraction melted, after crystallising successively from alcohol, acetone, and alcohol, at 202°; it depressed the melting points of the semicarbazones of the parent ketone (Found : C, 66·4; H, 8·9; N, 17·6. $C_{13}H_{21}ON_3$ requires C, 66·4; H, 8·9; N, 17·9%). The yield was 35%.

The ketone, 2-*ethyl*-2-Δ^1-cyclo*pentenyl*cyclo*pentanone*, regenerated from it had b. p. 140°/22 mm., $d_4^{22\cdot4°}$ 0·983385, $n_D^{22\cdot4°}$ 1·49756, $[R_L]_D$ 53·07 (calc., 52·92). It was oxidised with ozone in chloroform solution, the ozonide decomposed with hot water, and the product distilled in steam. The residue contained glutaric acid (m. p. 97° after recrystallisation), whilst the volatile fraction contained 2-ethyl*cyclo*pentanone, which was identified by means of its semicarbazone, m. p. 177° (Best and Thorpe, J., 1909, **95**, 713) (Found : C, 56·6; H, 8·8; N, 24·6. Calc. : C, 56·8; H, 8·9; N, 24·9%). These products were not those primarily formed, and if the ozonide was decomposed by means of cold water the greater part was converted into an oily *aldehyde* which was readily oxidised to the corresponding *acid* by silver oxide. This acid doubtless had the structure $CH_2<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CEt\cdot CO\cdot(CH_2)_3\cdot CO_2H\end{matrix}$, as it broke up into 2-ethyl*cyclo*pentanone and glutaric acid on merely boiling with water; it was too unstable to isolate in a pure state.

The ethylation of *cyclo*pentylidene*cyclo*pentanone was repeated with a specimen of the ketone regenerated from the semicarbazone; the same yield of the ethylation product was obtained.

Condensation with ethyl sodiocyanoacetate. This was carried out as described on p. 3105. The neutral reaction product contained, in addition to higher-boiling oils which were not investigated, a fraction, b. p. 164—165°/20 mm., consisting of a cyano-ester of the type (X) which was isolated in 10% yield (Found : C, 68·9, 68·8; H, 8·1, 8·1. $C_{15}H_{21}O_3N$ requires C, 68·4; H, 8·0%). Only a small quantity of acid material was produced in this reaction and this could not be purified.

The cyano-ester (3 g.) was boiled with baryta (15 g. in 75 c.c. of water) for 2 hours and the sparingly soluble barium salt produced

was collected and decomposed with ice-cold hydrochloric acid. The *acid* (type XI), isolated by means of ether, formed octahedral prisms, m. p. 135°, from acetone–benzene (Found: C, 68·4; H, 8·6. $C_{12}H_{18}O_3$ requires C, 68·6; H, 8·6%). The *semicarbazone* formed needles, m. p. 197°, from alcohol (Found: C, 61·0; H, 8·1. $C_{13}H_{21}O_3N_3$ requires C, 61·2; H, 8·2%).

2-iso*Propylidene*cyclo*pentanone* (III).

The ketone was prepared as described by Wallach (*Annalen*, 1912, **394**, 362); the use of dry sodium ethoxide was not found advantageous.

Semicarbazone. This was prepared and treated as before, but in spite of a careful search only one form was obtained, crystallising from methyl alcohol in large plates which became opaque on keeping; m. p. 217—218°. The ketone regenerated from it had b. p. 92°/20 mm., $d_4^{18\cdot4°}$ 0·96704, $n_D^{18\cdot4°}$ 1·49680, $[R_L]_D$ 37·70 (calc., 36·61).

Oxidation. The ozonide of this ketone gave, on decomposition, acetone (semicarbazone, m. p. 187°) and glutaric acid, m. p. 97°, which were identified in the usual ways.

Ethylation. This was carried out as described on p. 3107. Almost the whole of the ketone isolated boiled at 98—102°/22 mm., the yield of the new ketone being 90%. The *semicarbazone* formed stellate clusters of needles, m. p. 199°, from alcohol (Found: C, 63·3; H, 9·0. $C_{11}H_{19}ON_3$ requires C, 63·2; H, 9·1%). The ketone, 2-*ethyl*-2-iso*propenyl*cyclo*pentanone*, regenerated from it had b. p. 97—98°/20 mm., $d_4^{19\cdot7°}$ 0·94132, $n_D^{19\cdot7°}$ 1·47892, $[R_L]_D$ 45·84 (calc., 45·85). The structure of the ethylated ketone was established by oxidation with ozone in acetic acid solution by the method of Grignard (*Compt. rend.*, 1923, **177**, 669); the formation of formic acid was confirmed by the usual tests. The acetic acid solution was concentrated in a vacuum and then treated with semicarbazide, the *semicarbazone* of a ketonic *acid* being obtained; after three crystallisations from alcohol, it formed plates, m. p. 141—142° (Found: C, 52·3; H, 8·4. $C_{10}H_{19}O_3N_3$ requires C, 52·4; H, 8·3%). The acid was doubtless δ-acetylheptoic acid (Blaise and Köhler, *Compt. rend.*, 1909, **148**, 1403).

Condensation with ethyl sodiocyanoacetate. This was carried out as before. The *cyano*-ester, formed in 15% yield, had b. p. 135°/20 mm. (Found: C, 65·3; H, 8·0. $C_{13}H_{19}O_3N$ requires C, 65·8; H, 8·0%). On hydrolysis with baryta the ester yielded an *acid* (type XI) which crystallised from acetone–petroleum in long needles, m. p. 133° (Found: C, 65·4; H, 8·6. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%).

Camphorphorone.

The ketone was prepared in 40% yield by the method of Wallach and Collman (*Annalen*, 1904, **331**, 320) in the apparatus described by Day, Kon, and Stevenson (J., 1920, **117**, 639).

Semicarbazone. This derivative was formed very slowly, the mixture of ketone and semicarbazide being kept for 2 weeks before the first crop of semicarbazone was collected; further quantities separated when the mother-liquor was gradually diluted. The semicarbazone appears to exist in one form only, plates, m. p. 197—198° (Wallach and Collman, *loc. cit.*). The pure ketone regenerated from it had b. p. 87—88°/14 mm., $d_4^{18\cdot8°}$ 0·93722, $n_D^{18\cdot8°}$ 1·48511, $[R_L]_D$ 42·28 (calc., 41·23). The *pure* ketone combines rapidly with semicarbazide.

Oxidation. Oxidation with ozone gave acetone (semicarbazone, m. p. 187°) and α-methylglutaric acid, m. p. 77—78° (Found: C, 46·1; H, 6·5. Calc.: C, 46·1; H, 6·4%).

Ethylation. This operation was carried out as described on p. 3107. The semicarbazone of the ethylated ketone was obtained in 50% yield; the yield of ketone was doubtless higher. The *semicarbazone* crystallised from alcohol in stellate clusters of needles, m. p. 184° (Found: C, 64·4; H, 9·3. $C_{12}H_{21}ON_3$ requires C, 64·6; H, 9·4%). The ketone, *5-methyl-2-ethyl-2-isopropenylcyclopentanone*, regenerated from it had b. p. 95—96°/16 mm., $d_4^{18\cdot7°}$ 0·91131, $n_D^{18\cdot7°}$ 1·46533, $[R_L]_D$ 50·46 (calc., 50·47). The ketone was oxidised with ozone in acetic acid in the same way as the lower homologue. Formic acid was isolated, and a ketonic *acid* in the form of its *semicarbazone*, which crystallised from alcohol in plates, m. p. 147—148° (Found: C, 54·2; H, 8·7. $C_{11}H_{21}O_3N_3$ requires C, 54·4; H, 8·7%). The parent acid was doubtless *δ-acetyl-α-methylheptoic acid.*

Condensation with ethyl sodiocyanoacetate. Camphorphorone does not condense with ethyl sodiomalonate according to Vorländer (*loc. cit.*). The reaction with ethyl sodiocyanoacetate proceeded normally; the cyano-ester was not purified, the fractions 96—140°/15 mm. and 140—200°/15 mm. being directly hydrolysed with baryta to the nitrogen-free *acid* (type XI), which formed long needles, m. p. 135°, from acetone–benzene (Found: C, 66·5; H, 9·2. $C_{11}H_{18}O_3$ requires C, 66·7; H, 9·1%). The total quantity of acid obtained represented a 30% yield of condensation product.

Pulegone.

The ketone isolated from oil of pennyroyal by the bisulphite process had b. p. 99°/14 mm. and $[\alpha]_D$ + 20·8°.

The semicarbazone prepared from it consisted of one substance only and formed clusters of needles, m. p. 172°, after two crystal-

lisations from alcohol. A specimen of the ketone regenerated from it had b. p. 99°/14 mm., $d_{4^\circ}^{19\cdot2^\circ}$ 0·93712, $n_D^{19\cdot2^\circ}$ 1·48803, $[R_L]_D$ 46·78 (calc., 45·81) and $[\alpha]_D$ + 22·1°. On oxidation with ozone in chloroform solution, acetone and β-methyladipic acid, m. p. 94°, were obtained.

Methylation. This operation was carried out in ethereal solution with "molecular sodium," and a yield of about 50% of an oil, b. p. about 109°/20 mm., obtained after two distillations. The *semicarbazone* separated from alcohol in fine needles, m. p. 203—204° (Found: C, 64·5; H, 9·5. $C_{12}H_{21}ON_3$ requires C, 64·5; H, 9·5%). The ketone, 2 : 5-*dimethyl*-2-iso*propenyl*cyclo*hexanone* (2-*methyl*iso*pulegone*) (VII), had b. p. 108°/19 mm., $d_{4^\circ}^{18\cdot8^\circ}$ 0·92081, $n_D^{18\cdot8^\circ}$ 1·47163, $[R_L]_D$ 50·51 (calc., 50·47), and $[\alpha]_D$ (in alcohol) −122·1°.

The ketone was oxidised with ozone in acetic acid solution, formic acid and ε-acetyl-β-methylheptoic acid (Léser, *Bull. Soc. chim.*, 1901, **25**, 199) being obtained; the latter was isolated as its *semicarbazone*, which formed plates, m. p. 166—168° from dilute alcohol (Found: C, 54·2; H, 8·7. $C_{11}H_{21}O_3N_3$ requires C, 54·3; H, 8·7%).

Ethylation. This was carried out as before; the yield appeared to be about 40%. The *semicarbazone* of the new ketone was obtained in clusters of needles, m. p. 207—208° (Found: C, 65·7; H, 9·8. $C_{13}H_{23}ON_3$ requires C, 65·9; H, 9·7%). The ketone, 5-*methyl*-2-*ethyl*-2-iso*propenyl*cyclo*hexanone*, regenerated from it had b. p. 110°/15 mm., $d_{15^\circ}^{19\cdot1^\circ}$ 0·90362, $n_D^{19\cdot1^\circ}$ 1·46433, $[R_L]_D$ 55·05 (calc., 55·09), and $[\alpha]_D$ (in alcohol) − 174·0°.

Condensation with ethyl sodiocyanoacetate. This operation was carried out as before; both the neutral and the acid portion of the condensation product gave, on distillation, Vorländer's compound, m. p. 78°, the total yield being 42% (Found: C, 70·9; H, 7·8. Calc.: C, 71·2; H, 7·8%). Like the compound described on p. 3106, it forms, on treatment with sulphuric acid, an *imide* which forms needles, m. p. 129°, from alcohol and appears to be isomeric with the compound prepared by Vorländer (*loc. cit.*, p. 196) (Found: C, 74·5; H, 9·9; N, 7·2. $C_{12}H_{19}ON$ requires C, 74·6; H, 9·9; N, 7·2%).

iso*Pulegone.*

This ketone was prepared both from oil of pennyroyal and from pulegone hydrobromide. The crude ketone obtained from the latter source had b. p. 102—103°/16 mm., $d_{4^\circ}^{20\cdot4^\circ}$ 0·92761, $n_D^{20\cdot4^\circ}$ 1·46250, and $[\alpha]_D$ − 10·7°. A specimen obtained from oil of pennyroyal had b. p. 100—105°/17 mm., $d_{4^\circ}^{18\cdot3^\circ}$ 0·91024, n_D 1·46470, $[R_L]_D$ 46·18, and $[\alpha]_D$ + 36·7°. Both formed a semicarbazone crystallising in needles, m. p. 174°.

Methylation. This proceeded exactly as in the case of pulegone; the yield of the fraction, b. p. 104—107°/16 mm., was above 50%. Both natural and synthetic *iso*pulegone gave a strongly lævorotatory product from which the same semicarbazone, m. p. 203—204°, identical with that obtained from pulegone, was prepared. A small specimen of the ketone regenerated from it gave $[\alpha]_D$ in alcohol — 122·6°.

Condensation with ethyl cyanoacetate. The compound, m. p. 78°, obtained was identical with the compound prepared from pulegone; the yield was about the same in the two cases.

The authors' thanks are due to the Royal Society and the Chemical Society for grants which have defrayed the expense of this investigation.

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CCCCXVIII.—*The Mechanism of Kolbe's Electrosynthesis.*

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SINCE Kolbe's discovery of the production of ethane at the anode during the electrolysis of a solution of potassium acetate (*Annalen*, 1849, **69**, 279), many investigations have been made with a view to determine the nature of the undoubtedly complex process involved. Two rival theories have emerged: (1) The "oxidation" theory, which supposes that all the discharged anions react with water to give the acid, which is then oxidised by atomic oxygen to the synthetic product; and (2) the "discharged ion" theory, which supposes that two discharged anions unite directly. The following equations represent these reactions:

$$\left.\begin{array}{l} 2CH_3\cdot CO\cdot O\cdot + H_2O = 2CH_3\cdot CO_2H + O \quad . \quad . \quad . \quad . \quad . \quad (a) \\ 2CH_3\cdot CO_2H + O = CH_3\cdot CH_3 + 2CO_2 + H_2O \quad . \quad . \quad . \quad (a') \end{array}\right\}$$

$$2CH_3\cdot CO\cdot O\cdot = CH_3\cdot CH_3 + 2CO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

In two recent contributions to this subject (Gibson, J., 1925, **127**, 475; Robertson, *ibid.*, p. 2057) it is claimed that the oxidation theory has been proved to hold, not only for the ethane synthesis, but also for the Crum Brown and Walker synthesis of dibasic acids. The conclusions drawn in these papers do not seem to be entirely sound, and, moreover, fresh experimental evidence has now been obtained which demonstrates beyond all doubt that synthesis is due solely to the direct interaction of the discharged ions.

Concerning the intrinsic probability of the oxidation theory, it must be admitted that it would be somewhat surprising if the carboxylic hydrogen atom of a fatty acid were attacked by an oxidising agent in preference to the hydrogen atoms of the hydrocarbon residue, since one is accustomed to regard a carboxyl group as being very stable towards oxidising agents. The oxidation theory, in fact, could scarcely have been considered seriously had it not been shown by Gordon (*J. Physical Chem.*, 1914, **18**, 55) that comparatively large quantities of ethane and methane are formed when acetic acid is oxidised in dilute solution and at a moderate temperature with potassium persulphate.

Referring to the well-established fact that an anode of smooth platinum must acquire a definite potential before any appreciable quantity of ethane is formed, Gibson deduces that at this potential either (*a*) the acetate ion is first discharged, or (*b*) the acetic acid, in becoming oxidised to ethane, begins to act as a depolariser. This view requires some modification, since the so-called "discharging potential" of organic anions must, in reality, be a depolarisation potential. It may be assumed that the first reaction at the anode, *viz.*, the neutralisation of the electric charges on the ions, takes place with infinite velocity. Any subsequent chemical reactions in which the discharged ions may be involved, will, however, take place with a finite velocity dependent on the concentration of the reacting substances and on the temperature. Thus, no matter what views may be held as to the mechanism of ethane formation, there must necessarily exist in the neighbourhood of the anode an accumulation of the unstable substance $CH_3{\cdot}CO{\cdot}O{\cdot}$. Some at least of these discharged ions react with water, giving atomic oxygen. We thus have two unstable products at the anode, either of which may cause a back *E.M.F.* The point in the anode potential–current curve at which the current begins to increase rapidly is therefore the point at which these substances have attained concentrations sufficiently high to allow of their being removed with appreciable rapidity. This depolarisation may conceivably be effected in five ways :

(1) $O + O = O_2$.
(2) $2CH_3{\cdot}CO_2H + O = CH_3{\cdot}CH_3 + 2CO_2 + H_2O$.
(3) $CH_3{\cdot}CO_2H + 4O = 2CO_2 + 2H_2O$.
(4) $2CH_3{\cdot}CO{\cdot}O{\cdot} + 7O = 4CO_2 + 3H_2O$.
(5) $2CH_3{\cdot}CO{\cdot}O{\cdot} = CH_3{\cdot}CH_3 + 2CO_2$.

Gibson's second alternative is therefore capable of extension, and his conclusion that the particular reaction studied, *viz.*, the formation of trichloromethyl trichloroacetate, is an oxidation reaction

can scarcely be held as valid, since it is largely based on the fact that the potential at which this ester was observed to be first formed is not the discharging potential of the trichloroacetate ion.

Both Gibson and Robertson record a sharp fall in the amount of oxygen evolved in unit time at or about the synthetic potential, and entirely upon this evidence Robertson bases his conclusion that the synthesis of ethyl succinate is an oxidation reaction (*loc. cit.*, p. 2064). Such a fall was not observed by us. In any case, if equations (a) and (a′) be added together, equation (b) is obtained, *i.e.*, the amount of oxygen liberated must be independent of the mode of ethane formation. On either theory, the net result evidently is that one molecule of ethane is produced from two discharged ions without either liberating or using up any oxygen. The amount of evolved oxygen depends on the concentration of active oxygen at the anode, since it is produced by the reaction $O + O = O_2$. If with rising anode potential the amount of oxygen evolved in unit time decreases, the concentration of atomic oxygen must also be decreasing; but since the anode potential is rising, it cannot be the atomic oxygen alone which is responsible for the back *E.M.F.* observed—this must also be due to the discharged ions themselves.

Since the oxidation theory involves the partial oxidation of the acid, it is of interest to inquire to what extent complete oxidation to carbon dioxide and water takes place. Murray (J., 1892, **61**, 34) pointed out that the readiness with which complete oxidation takes place is inconsistent with the oxidation theory. From Robertson's figures it may be shown that about 30 to 40% of the oxygen developed at the anode is used for complete oxidation between the potentials of 2·02 and 2·30 volts, *i.e.*, *before* any synthesis commences. This theory therefore requires the extremely unlikely assumption that partial oxidation necessitates a higher potential (and therefore greater concentrations of reacting materials) than complete oxidation.

No positive evidence whatever would therefore appear to have been put forward in support of the oxidation theory. On the other hand, the recent work of Salauze (*Bull. Soc. chim.*, 1925, **37**, 522), who obtained good yields of ethane by electrolysis of a methyl-alcoholic solution of an acetate, proves that under these conditions the discharged ions do indeed interact directly.

In order to collect further data bearing upon the phenomenon of electrosynthesis, the electrolysis of solutions of acetates and propionates has been studied with regard to the effect of concentration and temperature of the solution, current density, anode potential, nature of solvent, and material of anode.

Experimental.

The apparatus used was of the same type as that employed by Gibson and by Robertson. The anode and cathode gases were collected together and transferred to a Bone and Wheeler gas-analysis apparatus by means of a Dittmar pipette filled with mercury. A complete analysis of each gas sample was made. The potentials given are on the hydrogen standard, and were obtained by calculation after direct comparison with a normal calomel electrode.

Experiments with Solutions of Potassium Acetate.—All acetate solutions were made *N* with respect to the free acid to prevent the solution becoming alkaline during the course of an experiment. *N*-Potassium acetate solution was electrolysed, three anodes of smooth platinum of different sizes being used with the same smooth platinum cathode. From Fig. 1 it will be seen that the values of *C.D.* and anode potential for all three anodes can be represented on one smooth curve, and that the ratio of ethane to hydrogen increases regularly with increasing anode potential independently of the size of the anode. Murray states (*loc. cit.*, p. 25) that "although the yield of ethane is increased by increasing the current or by employing a smaller anode, the variation is not to be accounted for by a change in current density alone. There are apparently some other factors influencing the electrolysis." The factor which Murray neglected appears to be the anode potential: between the limits of 2·7 volts, below which no formation of ethane takes place, and 3·0—3·1 volts, above which the yield of ethane can no longer be increased, the amount of ethane formed does increase with the *C.D.* When, however, the ethane : hydrogen ratio has reached its maximum value of nearly 0·9, the *C.D.* can be increased enormously without affecting the yield of ethane.

An increase in the concentration of the electrolyte scarcely affects the formation of ethane above 2·7 volts, as will be seen from the data obtained with a 3*N*-solution, which are shown graphically in Fig. 2. Ethane formation takes place, however, at somewhat lower anode potentials the more concentrated the solution, as is shown in Table I.

Table I.

Concentration	3*N*	4*N*	5*N*
Anode potential	2·68	2·66	2·62
$C_2H_6 : H_2$	0·11	0·11	0·12

The values of *C.D.* and of the ethane : hydrogen ratio for the two concentrations of acetate have been plotted against one another in Fig. 3. Up to *C.D.*'s of about 20 milliamp./sq. cm. the ratio

increases rapidly. These results indicate that a certain minimum concentration of discharged ionic products is necessary before any appreciable formation of ethane takes place.

A *N*-solution of potassium acetate was also electrolysed at 50° and 95°, the electrolysis cell being immersed in thermostats kept at these temperatures: an increase in temperature did not greatly influence the *P.D.* at which ethane formation commenced; as will be seen, however, from Fig. 2, the amount of ethane formed is less at the higher temperatures.

Experiments with Solutions of Potassium Propionate.—Preuner and Ludlam (*Z. physikal. Chem.*, 1907, **59**, 682) showed that with a 0·5*N*-solution of potassium propionate a polished platinum anode must acquire potentials of 2·58 volts and 2·70 volts, referred to a

FIG. 1.

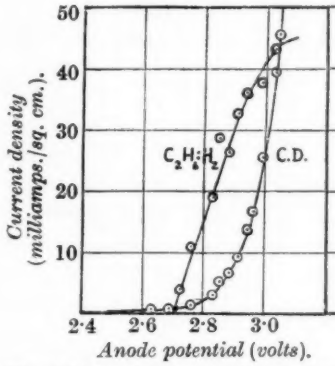
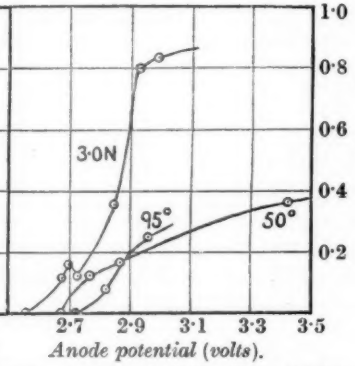


FIG. 2.



(*The right-hand scale of ordinates represents the ratio* $C_2H_6 : H_2$ *and relates to both diagrams.*)

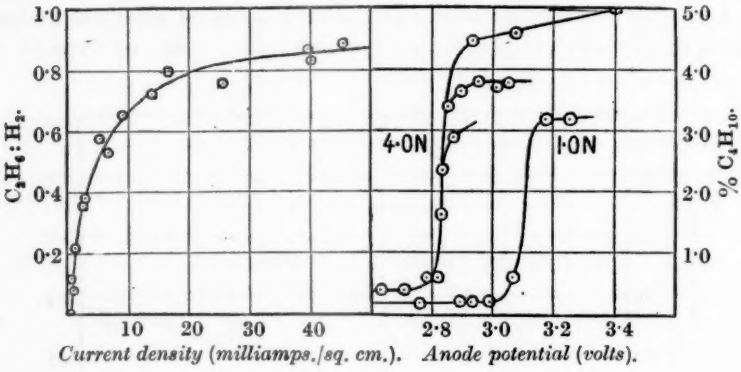
hydrogen electrode in the same solution as standard, for ethylene and butane formation, respectively. It seemed desirable to ascertain the effect of other factors on the products of electrolysis. All solutions were *N* with respect to free propionic acid.

N-Potassium propionate solution was electrolysed with smooth platinum electrodes. At low anode potentials, the gases evolved consisted mainly of hydrogen and oxygen with a little ethylene, but no butane. As the *P.D.* was raised the ethylene increased rapidly, reaching a maximum, after which butane made its appearance. Simultaneously with the increase of ethylene, the oxygen began to decrease, finally reaching a minimum. About 1% of carbon monoxide was always present. The results obtained with an anode of 7·2 sq. cm. surface are given in Table II. It is seen that the ethylene : hydrogen ratio begins to increase rapidly at 2·60 volts and tends to reach an asymptotic value of about 0·60

at 2·95 volts. Table III shows the results obtained with a 4*N*-solution using the same electrodes. The corresponding curve is of the same shape as with the *N*-solution, but is displaced 0·15 volt to the left, the ethylene formation commencing at a lower potential.

A *N*-solution was also electrolysed at 50°, using a smooth platinum anode of 0·165 sq. cm. surface. From Table IV it is seen that, although there is more ethylene at low potentials at this temperature, the increase with rise of anode potential is more gradual and the ethylene : hydrogen ratio does not increase much beyond 0·4.

FIG. 3. FIG. 4.



Current density (milliamps./sq. cm.). *Anode potential (volts).*

TABLE II.

N-Soln. at 10°. Anode = 7·2 sq. cm.				*N*-Soln. at 10°. Anode = 7·2 sq. cm.			
A.P.	*C.D.*	C_2H_4/H_2.	O_2/H_2.	*A.P.*	*C.D.*	C_2H_4/H_2.	O_2/H_2.
2·36	0·06	0·01	0·23	2·75	2·64	0·24	0·12
2·48	0·08	0·02	0·29	2·78	8·06	0·33	0·067
2·54	0·17	0·01	0·37	2·79	—	0·41	0·043
2·60	0·35	0·04	0·365	2·83	—	0·47	0·030
2·66	0·61	0·07	0·32	2·89	—	0·55	0·022
2·71	0·93	0·13	0·23	2·92	—	0·58	0·024

TABLE III.

4*N*-Soln. at 10°. Anode = 7·2 sq. cm.			
A.P.	*C.D.*	C_2H_4/H_2.	O_2/H_2.
2·35	0·01	0·01	0·37
2·46	0·07	0·03	0·36
2·54	0·13	0·10	0·30
2·60	0·31	0·29	0·14
2·63	0·82	0·43	0·047
2·71	5·56	0·58	0·018
2·75	8·33	0·59	0·011

TABLE IV.

N-Soln at 50°. Anode = 0·165 sq. cm.			
A.P.	*C.D.*	C_2H_4/H_2.	O_2/H_2.
2·56	2·7	0·04	0·28
2·63	6·1	0·09	0·24
2·68	12·1	0·16	0·17
2·75	28·5	0·25	0·10
2·79	46·1	0·28	0·077
2·86	84·8	0·34	0·055
2·95	158·2	0·38	0·042
3·07	249·7	0·40	0·031
3·15	304·2	0·41	0·029

Complete oxidation is, on the whole, more vigorous at 50° and also more free oxygen is evolved above 2·75 volts than at 10°. It appears that the increase of temperature increases the rate of reaction of the discharged ions with water more than it increases the rate of their interaction.

Fig. 4 shows the relation between the anode potential and the percentage of butane (after removal of carbon dioxide) for the two concentrations. With *N*-solution, butane begins to be formed in appreciable quantity at 3·05 volts and reaches a maximum of 3·2% at 3·15 volts. No greater quantity was obtained with *P.D.*'s up to 4·6 volts. With 4*N*-solution, three anodes were used, in order to cover the desired range of *C.D.*'s. The amount of butane increases suddenly at about 2·8 volts and reaches a maximum of 5·0% with the smallest anode. At 50°, no butane was formed even at high potentials.

Nature of the Anode Material.—A phenomenon which is somewhat difficult to explain is the profound influence of the anode material on synthesis in aqueous solution. In confirmation of the work of Preuner and Ludlam (*loc. cit.*, p. 689), it was found that at platinised platinum anodes no synthesis occurred with solutions of potassium acetate and of potassium propionate, although the presence of up to 10% of carbon dioxide showed that complete oxidation had taken place. With very large *C.D.*'s, small quantities of ethane and ethylene were obtained from the acetate and propionate solutions, respectively. In these cases, however, some of the platinum black had become detached and small spots of bright platinum were visible.

With gold anodes, we could detect no trace of synthetic product. With a *N*-solution of potassium acetate, the current increased regularly with increasing anode potential, whilst the gas evolved at 3·1 volts still consisted of hydrogen and oxygen with about 3% of carbon dioxide. The propionate solution gave a gas of similar composition at *P.D.*'s between 3 and 5·3 volts. The anode suffered considerable disintegration, and the solution became brown with dispersed gold.

Fichter and Krummenacher (*Helv. Chim. Acta*, 1918, **1**, 148) suggested that the ability of a metal to promote the Kolbe synthesis was connected with its oxygen overvoltage, and Gibson (*loc. cit.*, p. 484) also discusses this view. It seems more reasonable, however, to approach the problem from the point of view adopted by Preuner and Ludlam. The discharged ions may be supposed to react either with water to give acid and oxygen or with themselves to effect synthesis. Synthesis cannot occur unless there is a sufficient concentration of discharged ions at the anode. We are thus led to

the conclusion that the velocity of the reaction of discharged ions with water at surfaces of platinised platinum and of gold is much greater than at one of smooth platinum, so that their concentration does not attain a value sufficiently high to give synthesis.

Experiments with Non-aqueous Solvents.—The nature of the anode would be expected to have little effect when the solvent is such that reaction with the discharged ions cannot take place. Hofgartner (*Monatsh.*, 1911, **32**, 523) obtained ethane : hydrogen ratios as high as 0·97 by electrolysing an 8·8% solution of potassium acetate in glacial acetic acid with a smooth platinum anode. With the same anode material, Salauze (*loc. cit.*) obtained by electrolysis of acetates in methyl-alcoholic solution 95% of the possible ethane, and showed that in this solvent the nature of the anode, provided that it is not attacked, has much less influence than in aqueous solution.

The following experiment shows the effect of the addition of water on the electrolysis of 4·9 g. of potassium acetate and 1·52 g. of acetic acid in 100 c.c. of methyl-alcoholic solution. A platinised platinum anode of 0·165 sq. cm. surface and a smooth platinum cathode were used, and the current was maintained at the constant value of 25 milliamp. in each determination.

CH_3OH (c.c.)	100	95	90	80	0
H_2O (c.c.)	0	5	10	20	100
C_2H_6/H_2	0·71	0·58	0·22	0	0

It will be seen that ethane formation is inhibited by the presence of water. The way in which the effect due to the anode material is dependent on the solvent is further shown by electrolysing a solution of anhydrous sodium acetate in glacial acetic acid with an anode of (1) smooth platinum and (2) gold. The ratios of ethane to hydrogen in the evolved gases were 0·86 and 0·77, respectively. Synthesis therefore takes place readily at a gold anode in this solvent.

It has been shown that the yield of butane from the electrolysis of aqueous solutions of potassium propionate is very small. By using an anhydrous solvent, however, much better yields can be obtained. A *N*-solution of potassium propionate in equal volumes of methyl alcohol and propionic acid was electrolysed with a smooth platinum anode at 100 milliamp. until the liquid was saturated with the gases, which were then found in the following proportions : C_2H_4, 12·3; C_4H_{10}, 36·0; O_2, 0·5; CO, 0·5; H_2, 50·7%. A similar experiment with a gold anode gave a gas of approximately the same composition. It need scarcely be pointed out that this constitutes a valuable method for the preparation of butane.

We have stated that the bends in current–anode potential

curves must be due to depolarisation. Now in anhydrous solution this depolarisation must be effected exclusively by union of the discharged ions to give synthesis. It was therefore considered of interest to examine the electromotive phenomena at the anode under these conditions, and potential–current density curves were constructed for a smooth platinum anode in a methyl-alcoholic solution of potassium propionate (*N*) and propionic acid (*N*), care being taken to exclude traces of water. The propionate solution itself was used as a buffer solution between the cell and the potassium chloride solution leading to the calomel electrode. As shown in Fig. 5, depolarisation evidently occurs at 2·6—2·7 volts. Owing to the great solubility of the gases in methyl alcohol, it was not possible to obtain for analysis representative samples at the various anode potentials.

FIG. 5.

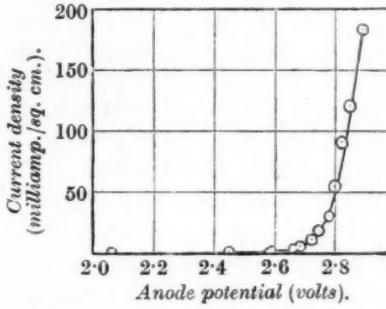
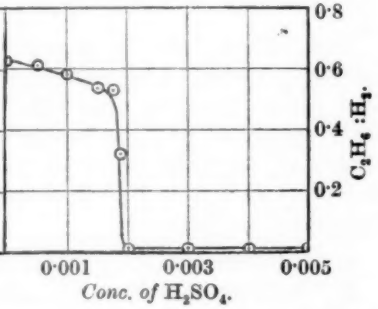


FIG. 6.



The Electrolytic Oxidation of Acetic Acid.—It might be held that, although the discharged ions interact in non-aqueous solutions, synthesis in aqueous solutions may be due either partly or entirely to oxidation of the free acid. It was thought that if in a solution of acetic acid the acetate ions could be prevented from discharging, whilst at the same time the oxidation conditions were maintained unaltered, it would be possible to ascertain conclusively whether or no ethane is obtained by oxidation of the acid. These conditions have been realised in the following experiment. A concentrated aqueous solution of acetic acid (15*N*) was electrolysed with the addition of varying small quantities of sulphuric acid, smooth platinum electrodes being used and a constant current of 35 milliamp. Each electrolysis was allowed to proceed for about 24 hours to ensure saturation of the liquid with the gases evolved.

The results are shown graphically in Fig. 6, in which the ethane : hydrogen ratio is plotted against the concentration of sulphuric acid in g.-equivs. per litre. It will be seen that the critical concentration of sulphuric acid is 0·002*N*, and that the formation of

ethane is then almost completely prevented. This concentration evidently corresponds to a critical concentration of discharged acetate ions, below which synthesis cannot take place. The ionisation of the acetic acid, already small owing to the high concentration of the solution, is still further reduced by the sulphuric acid; the current is then partly carried by the SO_4'' and HSO_4' ions. These, after discharge, react with water to give atomic oxygen, which, however, does not oxidise the acetic acid to ethane. Little oxygen was evolved in any of the experiments; it was used up in oxidising the acetic acid to carbon dioxide and water, 20—25% of carbon dioxide being present even in absence of ethane. This experiment shows beyond doubt that ethane is produced by the interaction of discharged acetate ions, and that electrolytic oxygen, when it oxidises acetic acid, does so completely and not partly.

Conclusion and Summary.

It is shown, both by a consideration of the work of previous investigators and by the presentation of fresh experimental evidence, that the phenomena observed in the electrolysis of solutions of fatty acids can only be accounted for on the "discharged ion" theory as originally proposed by Crum Brown and Walker. The reactions in which the discharged ions take part may now be formulated as follows:

1. $2R{\cdot}CO{\cdot}O{\cdot} + H_2O = 2R{\cdot}CO_2H + O$ (Faraday reaction).
2. $2R{\cdot}CO{\cdot}O{\cdot} = R{\cdot}R + 2CO_2$ (Synthetic reaction).
3. $2R{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot} = R{\cdot}CH_2{\cdot}CO_2H + (R - H){:}CH_2 + CO_2$ (Unsaturated product).
4. $2R{\cdot}CO{\cdot}O{\cdot} = R{\cdot}CO_2R + CO_2$ (Ester formation).
5. $R{\cdot}CO{\cdot}O{\cdot} + OH = R{\cdot}OH + CO_2$ (Alcohol formation).
6. $R{\cdot}CO{\cdot}O{\cdot} + nO = xH_2O + yCO_2$ (Complete oxidation).

The conditions which favour reactions 2 and 3 are precisely those which retard or prevent reaction 1.

The main points which have been put forward in support of the above theory may be summarised as follows:

1. The arguments advanced by Gibson and by Robertson in favour of the oxidation theory are largely fallacious.

2. The electrolytic oxidation of acetic acid has been shown to be complete and not partial under ordinary conditions. Complete oxidation takes place to a considerable extent at low anode potentials.

3. The presence of a definite concentration of the discharged anions themselves is indispensable for synthesis.

4. In confirmation of the results of other workers, it has been

shown that synthesis can and does take place in non-aqueous solutions to which the oxidation theory is not applicable.

The authors wish to thank Professor Sir James Walker, F.R.S., for his helpful criticism and advice during the course of this work, and also Messrs. Brunner Mond and Co., Ltd., for a grant which defrayed part of the expense incurred.

UNIVERSITY OF EDINBURGH. [*Received, September 11th*, 1926.]

CCCCXIX.—*Optical Activity dependent on Co-ordinated Beryllium, Copper, and Zinc.*

By WILLIAM HOBSON MILLS and REGINALD ARTHUR GOTTS.

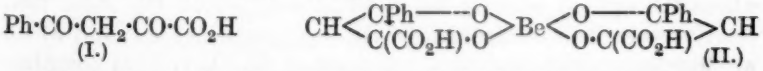
IT was observed by Lowry and Burgess, in an examination of the properties of the metallic derivatives of benzoylcamphor (J., 1924, **125**, 2081), that beryllium benzoylcamphor when dissolved in benzene, chloroform, and other solvents showed mutarotation, and they referred this mutarotation to the gradual disappearance in solution of optical activity associated with the beryllium, since, as they pointed out, the beryllium atom in this compound would probably act as a centre of asymmetry in the same way as the central carbon atom of the ketodilactone of benzophenonetetracarboxylic acid (Mills and Nodder, J., 1920, **117**, 1407; 1921, **119**, 2094).

The experiments described in the present paper were carried out with the object of obtaining direct experimental proof that a dissymmetrically linked beryllium atom can, as thus indicated, give rise to optical activity.

We endeavoured to find a β-diketone, containing a salt-forming group, which would be itself devoid of molecular dissymmetry, but could be shown to acquire it on conversion into its beryllium derivative. Experiments directed towards the same end, which, however, did not yield positive results, have recently been described by Morgan and Porter (this vol., p. 1256).

After some exploratory work, we found in benzoylpyruvic acid (I) a compound with which this plan could be carried out.

Aqueous solutions of the sodium salt of this acid dissolved freshly-precipitated basic beryllium carbonate, the *sodium* salt of the beryllium derivative (II) * being formed.



* The linkings in the six-membered rings in this formula are represented by single lines with the intention of indicating that the question of the nature of these bonds is left open, though we regard the beryllium atom as being linked to the four oxygen atoms in the way suggested by Sidgwick (J., 1923, **123**, 725

But while this salt crystallised well and reacted immediately with the mineral acid salts of the common alkaloids to give sparingly soluble alkaloid salts of the beryllium complex, the latter compounds could not be obtained crystalline in this manner. The alternative method of preparation was therefore tried of digesting the alkaloid salts of benzoylpyruvic acid in alcoholic solution with basic beryllium carbonate and by this means the *brucine* salt of the beryllium complex could be obtained in crystalline form without difficulty after crystalline nuclei had (with some little trouble) once been obtained.

The brucine salt crystallised with 8 molecules of water of crystallisation and was sufficiently soluble in aqueous alcohol for polarimetric examination, but no mutarotation could be observed in this solvent. It was realised, however, that any activity associated with the co-ordinated beryllium was likely to be exceedingly evanescent and that under these conditions the expected mutarotation might well have proceeded to completion before any observations could be taken. The salt was therefore dehydrated. The anhydrous compound proved to be exceedingly soluble in chloroform and moderately soluble in absolute alcohol and with these solutions we were able to observe changes of rotation of the type expected.

The solution of the anhydrous brucine salt in chloroform showed a very rapid mutarotation. Three minutes after wetting, the salt showed a specific rotation $[\alpha]_{5461}$ of $+ 25{\cdot}0°$, which decreased according to the unimolecular law and reached a steady value of $+ 5{\cdot}0°$ within about $\frac{1}{2}$ hour.

In alcohol, only very fleeting mutarotations were at first observed, but by taking greater and greater care in purification of the solvent, and by employing vessels of silica, the time required for the completion of the mutarotation was at length increased to 3 hours, the specific rotation $[\alpha]_{5461}$ decreasing during this period from $39{\cdot}9°$ (observed 5 minutes after first wetting the salt) to the final value $13{\cdot}1°$.

Crystallisation of the brucine salt from aqueous alcohol thus gives a dextrorotatory salt the optical activity of which *decreases* in solution to a limiting value, and which is accordingly, on the hypothesis on which we were working, the brucine salt of the *d*-beryllium complex.

We also obtained the salt in an initially lævorotatory form in which the optical activity *increased* in solution to the same final positive value as was attained by the dextrorotatory salt and which we therefore regarded as the brucine salt of the *l*-beryllium complex. This modification was obtained by dissolving the anhydrous brucine *d*-acid salt in chloroform, allowing the solution to stand for 2 hours to racemise the beryllium complex, and then precipitating the salt

in two fractions by adding ether. The first fraction consisted principally of the original initially dextrorotatory salt, but the second fraction showed in chloroform an initial lævorotation $[\alpha]_{5461}$ of $-11{\cdot}8°$, which rose in 25 minutes to $+ 5{\cdot}2°$ and this fraction was therefore regarded as the diastereoisomeric salt, brucine *l*-berylliobenzoylpyruvate.

The brucine salt had thus been obtained in two modifications showing opposite and (within the degree of approximation to be expected) equal mutarotations. It was then necessary to prove that these mutarotations were in fact due, as had been provisionally assumed, to the disappearance of an optical activity associated with the beryllium, for whilst brucine salts are lævorotatory in aqueous solution, a not inconsiderable number of the salts of this alkaloid with organic acids are dextrorotatory in organic solvents—for example, brucine benzoylpyruvate is dextrorotatory in chloroform or alcoholic solution. The rotatory power of brucine in its salts in solution in organic solvents is thus particularly sensitive to the acid with which it is associated, and, in the absence of proof to the contrary, the possibility would always remain that the observed mutarotation was due to the effect of tautomeric changes in the berylliobenzoylpyruvic acid on the optical activity of the brucine with which it was combined. To obtain this proof it was necessary to remove the brucine without destroying the very delicate optical activity depending on the co-ordination of the beryllium.

It appeared that this removal of the brucine could be most simply effected (and with sufficient completeness) by taking advantage of the sparing solubility of brucine hydrochloride in absolute alcohol, but in trying this method we were met with the difficulty that most of the salts of berylliobenzoylpyruvic acid are also sparingly soluble in this solvent. The dimethylammonium salt proved, however, to be sufficiently soluble for our purpose.

Brucine *d*-berylliobenzoylpyruvate was therefore added to a very carefully purified alcoholic solution of a considerable excess of dimethylamine hydrochloride. A precipitate formed which proved to be mainly brucine hydrochloride and had slightly more than the theoretical weight. The filtrate (observed as rapidly as possible) showed a dextrorotation, $\alpha_{5461} + 1{\cdot}13°$ ($l = 2$), which, as was to be expected, was evanescent and sank to zero in about $\frac{1}{4}$ hour. The solution finally became faintly lævorotatory ($- 0{\cdot}1°$), indicating the presence of a small amount of unremoved brucine hydrochloride. On evaporation, it left a crystalline residue from which analytically pure *dimethylammonium berylliobenzoylpyruvate* was isolated.

A similar experiment was made with the diastereomeric brucine *l*-acid salt. The solution showed, after the removal of the greater

part of the brucine, a lævorotation α_{5461} of $-0{\cdot}63°$ which rose in 10 minutes to a final value of $-0{\cdot}06°$.

Thus the greater part of the brucine could be removed from these solutions without a corresponding decrease in their unstable optical activity. This activity must therefore be a property of beryllio-benzoylpyruvic acid and the molecule of this substance must be dissymmetric.

These observations show in the first place that the beryllium derivatives of the β-diketones are not simple beryllium salts of the enolic forms, $(R{\cdot}CO{\cdot}CH{:}CR{\cdot}O)_2Be$, since a beryllium derivative of benzoylpyruvic acid thus constituted could not exist in enantiomorphous modifications. They accordingly provide a new proof that these compounds are internally complex salts in which both oxygen atoms in each of the two diketone residues are directly linked to the beryllium atom as shown in formula (II).

FIG. 1.

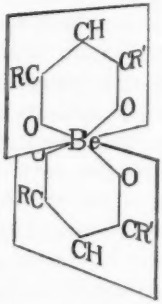
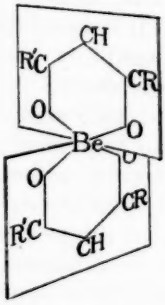


FIG. 2.



Moreover, to give dissymmetry of the molecule, the planes of the two rings between which the beryllium atom is shared must intersect as represented in Figs. 1 and 2.

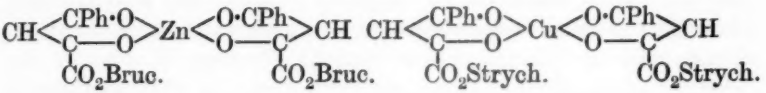
The four oxygen atoms to which the beryllium atom is linked must therefore be disposed tetrahedrally about it.

The arrangement of the attached atoms about the 4-co-ordinated beryllium atom, which these experiments establish for the dissolved molecule, thus corresponds with that deduced for the crystalline state by Bragg and Morgan from their study of the crystal structures of basic beryllium acetate (*Proc. Roy. Soc.*, 1923, *A*, **104**, 437).

After it had been shown that the mutarotation of the salts of berylliobenzoylpyruvic acid was due to the disappearance of an optical activity associated with the co-ordinated beryllium atom, we sought for evidence of the existence of optical activity similarly associated with other metals and found that analogous zinc and copper compounds showed a corresponding behaviour.

It proved possible to obtain the *copper* derivative of strychnine

benzoylpyruvate and the *zinc* derivative of brucine benzoylpyruvate in crystalline form. Both these compounds, when anhydrous, are soluble in chloroform and their solutions showed definite mutarotations.



For example, a chloroform solution of the zinc derivative gave an initial rotation, α_{5461}, of $+ 0{\cdot}90°$ which sank in about a $\frac{1}{4}$ hour to $+ 0{\cdot}18°$. The copper derivative was difficult to examine polarimetrically on account of the colour of its solutions. The zone of maximum transparency (λ 5100—λ 5200) of the chloroform solution, however, lies not very far from the green mercury line (λ 5461) and in this light it was possible to get satisfactory measurements on 0·7—0·8% solutions in a 2-dcm. tube. Although, with such dilute solutions, the readings were necessarily small, the evidence for the mutarotation was quite definite. Thus in one experiment, the observed rotation, α_{5461}, fell in $\frac{1}{2}$ hour from $+ 0{\cdot}39°$ to $+ 0{\cdot}06°$, the limit of observational error being about 0·03°.

As the optical behaviour of these zinc and copper compounds resembles so closely that of the corresponding beryllium compound, we think it justifiable to conclude that the changes observed in their rotatory powers are due to the corresponding cause, namely, the disappearance of unstable optical activity associated with the co-ordinated zinc and copper atoms.

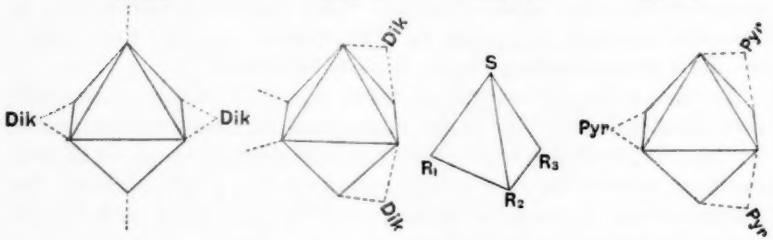
From the existence of this activity it is accordingly to be concluded that in these compounds the 4-co-ordinated metallic atoms and the four oxygen atoms to which each is attached do not lie in one plane.

This is of special interest in view of the fact that both copper and zinc are capable of forming compounds in which their co-ordination number is six. If the view is adopted that there are six fixed octahedrally disposed positions about these atoms in which alone other atoms can be attached, then the 4-co-ordinated compounds of zinc and copper must have either (1) the planar configuration (Fig. 3), in which the two vacant positions corresponding with the two latent valencies are at the ends of a diagonal, or (2) the configuration represented in Fig. 4, in which the vacant positions are on one edge of the octahedron.

Configuration (1), which corresponds with that assigned by Werner to the 4-co-ordinated compounds of platinum, and with that which, according to the observations of Vernon, belongs to the isomeric dimethyltellurium di-iodides (J., 1920, **117**, 86, 889), is excluded by

our observations. Configuration (2), moreover, would seem improbable on general grounds, since it is difficult to see why the molecule should assume the form conditioned by this distribution of the valencies when the planar configuration, which would apparently give a so much better balanced system, was also possible. Although too much weight must not be assigned to considerations of this kind in view of the uneven distribution in space of the valencies of the doubly-linked nitrogen atom, as well as those of the sulphur in the thionyl radical (Phillips, J., 1925, **127**, 2552; Harrison, Kenyon, and Phillips, this vol., p. 2079), the most probable inference to be drawn from these observations would seem to be that the valencies of copper and zinc have not the same direction in compounds in which their co-ordination number is four as in those in which it is six. That is to say, when two of the valencies of the 6-co-ordinated atoms of these metals become latent, this change is accompanied by a change in the directions of the four

FIG. 3. FIG. 4. FIG. 5. FIG. 6.



valencies which remain active in the resulting 4-co-ordinated compounds, these four assuming a "tetrahedral" arrangement, so that it is most probable that in the molecules of the zinc and copper derivatives of the β-diketones, as in those of their beryllium derivatives, the four oxygen atoms are disposed tetrahedrally about the metallic atom.

In the case of arsenic, a similar difference of valency direction must exist in the compounds of the co-ordination numbers four and six. In *p*-carboxyphenylmethylethylarsine sulphide, a compound of the type $R_1R_2R_3AsS$, resolved by one of us and R. Raper (J., 1925, **127**, 2479), the valencies have evidently a tetrahedral distribution (Fig. 5), whilst in tripyrocatechylarsenic acid, which was obtained in optically active forms by Rosenheim and Plato (*Ber.*, 1925, **58**, 2000), the valencies must be octahedrally disposed (Fig. 6).

EXPERIMENTAL.

Sodium Berylliobenzoylpyruvate, $Be(C_{10}H_6O_4Na)_2,H_2O$.—A solution of sodium benzoylpyruvate (Brömme and Claisen, *Ber.*, 1888,

21, 1131) in 10—12 parts of water is digested on the water-bath with the equivalent quantity of freshly-precipitated basic beryllium carbonate. The latter dissolves and, on cooling, the *sodium* salt of the beryllium derivative crystallises. Recrystallised from hot water, aqueous alcohol, or acetone, it forms slender needles containing one molecule of water of crystallisation (Found : Be, 1·9; Na, 10·2; H_2O, 4·25. $C_{20}H_{12}O_8Na_2Be,H_2O$ requires Be, 2·0; Na, 10·15; H_2O, 4·15%).

Brucine d-*Berylliobenzoylpyruvate*, $Be(C_{10}H_7O_4,C_{23}H_{26}O_4N_2)_2,8H_2O$. —Benzoylpyruvic acid (12·6 g.) and brucine (28 g.) were dissolved in warm alcohol (100 c.c.). The yellow solution was diluted with water (50 c.c.) and moist freshly-precipitated beryllium carbonate (from 5·4 g. of crystallised beryllium sulphate) was gradually stirred in. The carbonate dissolved slowly (15—20 minutes). The solution, acidified with a drop of glacial acetic acid, was filtered, allowed to cool slowly, and while still warm inoculated with a few crystals of brucine berylliobenzoylpyruvate previously obtained by slow cooling and scratching. The compound was deposited in crystalline form and was obtained by recrystallisation from warm 80% alcohol as clusters of pale yellow needles. It was completely dehydrated without losing its crystalline form by standing in a high vacuum over phosphorus pentoxide for 3 weeks in the cold, or by heating at 95—100°/20 mm. for 8 hours. The anhydrous salt melts at 212—215° (decomp.) and is very soluble in chloroform and rather sparingly soluble in absolute alcohol (Found : C, 66·9; H, 5·7; Be, 0·8. $C_{66}H_{66}O_{16}N_4Be$ requires C, 67·1; H, 5·6; Be, 0·8%. Found : H_2O, 10·6. $8H_2O$ requires 10·9%).

Mutarotation of Brucine d-*Berylliobenzoylpyruvate*.—(a) *In chloroform.* A solution of the salt (1·058 g.) in chloroform (17·34 g.) showed at 20° the following rotations ($l = 2$) ($[\alpha]^{20°}_{5461} = +25·06°$ and $+5·00°$ for $t = 3$ and ∞, respectively) :

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·0508).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·0508).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·0508).
3	+4·26°	(4·26°)	12	2·04°	2·04°	21	1·27°	1·27°
4	3·86	3·88	13	1·90	1·91	32	0·96	0·97
5	3·40	3·55	16	1·58	1·60	34	0·86	0·94
7	2·98	2·99	17	1·52	1·51	∞	0·85	(0·85)
8	2·76	2·75	18	1·45	1·44			

The numbers in the first column give the time in minutes from the first wetting of the salt. Those in the third column are calculated from the formula for the unimolecular reaction,

$$\log_{10}(\alpha_0 - \alpha_\infty)/(\alpha_t - \alpha_\infty) = kt,$$

substituting for α_0 and α_∞ the observed values 4·26° and 0·85° and giving k the value 0·0508. Their agreement with the observed

numbers indicates that the mutarotation proceeds in accordance with the unimolecular law.

(b) *In alcohol.* A solution of the salt (0·4200 g.) in absolute alcohol made up to a volume of 50 c.c. at 20° showed the following rotations ($l = 4$) ($[\alpha]^{20°}_{5461} = +39·9°$ and $+13·1°$ for $t = 5$ and ∞, respectively):

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·0094).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·0094).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·0094).
5	+1·34°	(1·34°)	30	0·96°	0·96°	150	0·46°	0·48°
7	1·30	1·30	60	0·73	0·71	∞	0·44	(0·44)
10	1·20	1·25	90	0·60	0·58			
20	1·09	1·09	120	0·50	0·51			

The correspondence between the observed values and those calculated from the above formula (column iii) shows that in this solvent also the mutarotation proceeds in accordance with the unimolecular law. As has been explained, the relative rate is greatly dependent on the purity of the solvent; in alcohol of the purity that we were able to obtain,* it was much slower than in chloroform ($k = 0·0094$ for alcohol as against 0·0508 for chloroform).

Brucine l-*Berylliobenzoylpyruvate.*—A solution of anhydrous brucine *d*-berylliobenzoylpyruvate (8 g.) in anhydrous chloroform (25 c.c.), after being kept for 2 hours, was cooled to —5°, and ether (40 c.c.) added. On vigorous shaking, a part of the salt (4·5 g.) was deposited as a microcrystalline mass which mostly adhered to the sides of the vessel. The mother-liquor was quickly filtered into more ether (100 c.c.); a second fraction of the salt (2·6 g.) was then precipitated.

The first fraction consisted chiefly of brucine *d*-berylliobenzoylpyruvate, since a solution of 1·166 g. in chloroform (18·655 g.) gave the following rotations ($l = 2$) ($[\alpha]^{20°}_{5461} = +15·8°$ and $+5·2°$ for $t = 3$ and 26, respectively):

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·053).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·053).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·053).
3	+2·75°	(2·75°)	7	2·00°	2·04°	13	1·44°	1·45°
4	2·51	2·54	8	1·94	1·91	20	1·05	1·13
5	2·39	2·35	9	1·80	1·79	26	0·90	(0·90)
6	2·20	2·18	11	1·59	1·60		(final value)	

The second fraction showed, however, a strong initial lævorotation and was *brucine* l-*berylliobenzoylpyruvate* (Found: C, 66·7; H, 5·55; Be, 0·7. $C_{66}H_{66}O_{16}N_4Be$ requires C, 67·1; H, 5·6; Be, 0·8%).

Mutarotation of brucine *l*-berylliobenzoylpyruvate in chloroform: A solution of the anhydrous salt (0·6334 g.) in chloroform (20·70 g.)

* The alcohol was first dried over lime, then over calcium, and finally distilled from a little silver nitrate to remove ammonia.

gave the following rotations ($l = 2$) ($[\alpha]^{20°}_{5461} = -11·8°$ and $+5·0°$ for $t = 2$ and 25, respectively) :

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·076).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·076).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·076).
2	−1·04°	−(1·04°)	8	0·00°	−0·08°	20	+0·41°	+0·38°
2½	0·93	0·92	10	+0·16	+0·07	22	0·43	0·39
4	0·60	0·60	12	0·19	0·18	25	0·44	(0·42)
5	0·46	0·44	14	0·24	0·26			
7	0·32	0·18	17	0·35	0·33			

Optically Active Solutions of Dimethylammonium Berylliobenzoylpyruvate.—(1) *The dextrorotatory salt.* Dimethylamine hydrochloride (0·36 g.; 4 mols.), dried over phosphorus pentoxide, was dissolved in carefully purified alcohol (50 c.c.) in a silica flask at 20°. Finely-powdered anhydrous brucine *d*-berylliobenzoylpyruvate (1·97 g.) was added, and the mixture well shaken. Brucine hydrochloride began to separate after a few seconds and as soon as the precipitation was finished (usually in 60—90 seconds) the solution was forced by gentle air-pressure through a dry asbestos filter directly into a 2-dcm. silica polarimeter tube and observations were taken as rapidly as possible. The weight of crude brucine hydrochloride collected on the filter was 1·5 g. (calc., 1·44 g.).

With the above-mentioned quantities the following polarimetric observations were made :

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·095).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·095).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k =$ 0·095).
2	+1·13°	+(1·11°)	7	0·29°	0·31°	13	+0·03°	+0·01°
3	0·83	0·87	8	0·23	0·23	14	0·00	−0·01
4	0·68	0·68	9	0·16	0·16	15	−0·08	−0·03
5	0·52	0·53	10	0·10	0·11	16	−0·10	—
6	0·40	0·40	11	0·10	0·07		(final value)	

After the completion of the polarimetric observations, the whole of the filtrate was allowed to evaporate. The crystalline residue was washed with a very little cold water to remove the excess of dimethylamine hydrochloride and then crystallised from dilute alcohol to remove the small amount of brucine hydrochloride which was left in the original solution and to which the final lævorotation was due. *Dimethylammonium berylliobenzoylpyruvate* was thus obtained as small, nearly colourless prisms, m. p. 95—96° (Found : N, 5·9; Be, 1·9. $C_{21}H_{23}O_8N_2Be$ requires N, 5·8; Be, 1·9%). The salt is moderately soluble in absolute, easily soluble in dilute alcohol. It is not hygroscopic, but is easily hydrolysed in presence of water with the formation of acetophenone.

(2) *The lævorotatory salt.* Brucine *l*-berylliobenzoylpyruvate (1 g.) was digested with a solution of dimethylamine hydrochloride

(0·24 g.) in carefully purified alcohol (31·5 c.c.). After the separation of the brucine hydrochloride was finished, the mixture was filtered and the following polarimetric observations were made on the filtrate ($l = 2$):

t (mins.).	$a^{20°}_{5461}$.	a calc. (k= 0·164).	t (mins.).	$a^{20°}_{5461}$.	a calc. (k= 0·164).	t (mins.).	$a^{20°}_{5461}$.	a calc. (k= 0·164).
2	−0·63°	(0·63°)	5	0·30°	0·24°	9	0·10°	0·10°
3	0·42	0·45	7	0·15	0·15	10	−0·06	0·09
4	0·36	0·33	8	0·10	0·12		(final value)	

Strychnine Cupribenzoylpyruvate.—An alcoholic solution of strychnine benzoylpyruvate was prepared by dissolving finely-powdered strychnine (6·6 g.) in a solution of benzoylpyruvic acid (4·2 g.) in alcohol (50 c.c.). To this was added, drop by drop, a solution of cupric acetate (1·82 g.) in warm dilute alcohol (15 c.c.). A further quantity of strychnine (3—4 g.) was then added to take up part of the acetic acid liberated in the reaction. After long standing in the cold, the green, alcoholic solution deposited the *strychnine* salt of the cupri-derivative of the acid in small, dark green prisms containing 4 mols. of water of crystallisation, m. p. (decomp.) 97—98°. The salt is insoluble in water, benzene, or ether and sparingly soluble in aqueous alcohol or acetone. It can be recrystallised from warm dilute alcohol or acetone containing a trace of acetic acid to prevent the hydrolytic decomposition which otherwise takes place.

It was dehydrated by heating for 6—8 hours at 80°/80 mm. over phosphorus pentoxide. The anhydrous salt is readily soluble in chloroform. (Found for anhydrous salt: C, 66·6; H, 5·3; Cu, 5·6. $C_{62}H_{58}O_{12}N_4Cu$ requires C, 66·8; H, 5·2; Cu, 5·7%. Found for hydrated salt: H_2O, 5·6. Calc. for $4H_2O$: H_2O, 5·5%).

Mutarotation.—(1) A solution of the anhydrous salt (0·0826 g.) in chloroform (17·30 g.) showed the following rotations:

t (mins.).	$a^{20°}_{5461}$.	a calc. (k=0·067).	$[a]^{20°}_{5461}$.
3	+0·39°	(0·39°)	+27·6°
7	0·23	0·24	—
14	0·13	0·12	—
30	0·06 (final value)	0·065	4·2

(2) A solution of the anhydrous salt (0·0877 g.) in chloroform (17·654 g.) showed the following rotations:

t (mins.).	$a^{20°}_{5461}$.	a calc. (k=0·067).	$[a]^{20°}_{5461}$.
5	+0·23°	(0·23°)	+15·6°
7	0·17	0·18	—
11	0·12	0·13	—
15	0·10	0·10	—
24	0·06 (final value)	0·06	4·1

Brucine Zincibenzoylpyruvate.—An aqueous alcoholic solution of brucine benzoylpyruvate, prepared from benzoylpyruvic acid (4·2 g.), brucine (9·2 g.), alcohol (50 c.c.), and water (10 c.c.) was boiled gently for 15 minutes with the equivalent quantity of moist freshly-precipitated basic zinc carbonate. The deep yellow liquid was filtered hot, and the filtrate was allowed to cool after the addition of a few drops of acetic acid. A pale yellow, gelatinous mass, in which a zinc salt as well as the brucine salt of zincibenzoylpyruvic acid was present, was precipitated. In order to obtain the latter compound the precipitate (10 g.) was collected, dried, and extracted with chloroform (50 c.c.) for ½ hour in a Soxhlet apparatus. The yellow solution, evaporated, left a gum (1·8 g.) which was dissolved in warm alcohol containing a little acetic acid. This solution, filtered and allowed to stand, deposited *brucine zincibenzoylpyruvate* as a mass of microscopic, yellow needles decomposing at 185°.

The salt dissolves readily in warm dilute alcohol but is easily hydrolysed with the formation of acetophenone (Found: Zn, 5·4. $C_{66}H_{66}O_{16}N_4Zn$ requires Zn, 5·3%).

Mutarotation.—The following polarimetric observations were made in a 2-dcm. tube on a solution prepared from the dehydrated salt (0·3167 g.) and chloroform (20·70 g.):

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k=0·082$).	$[\alpha]^{20°}_{5461}$.
2	+0·90°	(0·90°)	+20·1°
4	0·74	0·67	—
6	0·52	0·52	—
10	0·33	0·34	—
15	+0·18 (final value)	0·24	+ 4·0

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[*Received, October 28th,* 1926.]

CCCCXX.—*The Unsaponifiable Matter from the Oils of Elasmobranch Fish. Part II. The Hydrogenation of Squalene in the Presence of Nickel.*

By ISIDOR MORRIS HEILBRON, THOMAS PERCY HILDITCH, and EDWARD DAVID KAMM.

SQUALENE has already been hydrogenated by Tsujimoto (*Ind. Eng. Chem.*, 1916, **8**, 889) and by Chapman (J., 1917, **111**, 56; 1923, **123**, 769), the former using a platinum catalyst and a solution of squalene in ether under pressure, the latter a platinum catalyst and squalene alone at 190° and atmospheric pressure. Both authors appear to have obtained the same dodecahydrosqualene; the physical contants of their products are in good agreement with each other, and

with those of the product now obtained by us using a nickel catalyst. We regard the obvious similarity of the completely hydrogenated hydrocarbons as conclusive evidence of the identity of squalene and spinacene (Heilbron, Kamm, and Owens, this vol., 1630).

The Physical Constants of Completely Hydrogenated Squalene.

Constant.	Chapman.	Tsujimoto.	Present authors.
B. p.	280—281°/24 mm.	274°/10 mm.	224—226°/3 mm.
$n_D^{20°}$	1·4532	1·4525	1·4534
$d_{20°}^{20°}$	0·8119	0·8125 (at 15°/4°)	0·8107
$[R_L]_D$ (M = 422)	140·6	—	140·9

The hydrogenation of squalene does not, however, appear to have been studied from the point of view of selective attachment of hydrogen at the ethenoid linkings. Work in recent years has indicated that in the majority of cases where there is more than one double bond present in the molecule, the course of hydrogenation is definitely selective. An observation which is somewhat pertinent to the present case is that of Richardson, Knuth, and Milligan (*Ind. Eng. Chem.*, 1925, **17**, 80), who state that the highly unsaturated glycerides of the eicosanoic series present in whale oil are hydrogenated to the diethenoid derivatives before any fully saturated glyceride is produced.

The case of squalene is especially interesting, since it is an aliphatic hydrocarbon containing thirty carbon atoms and six ethenoid linkings. The method of hydrogenation which we have employed is to treat the oil with pure hydrogen at 130—160° in the presence of a nickel catalyst under the general conditions described by E. F. Armstrong and one of us (*Proc. Roy. Soc.*, 1919, *A*, **96**, 137; 1920, *A*, **98**, 27; 1925, *A*, **108**, 121), employing a similar type of apparatus and measuring the absorption of hydrogen continuously as therein described.

The results have proved that the hydrogenation is strongly selective and there is clear evidence that the saturation of each double bond takes place to a large extent consecutively. At the same time, a preliminary examination of the products which have been hydrogenated until only one ethenoid linking remains, indicates that a mixture of monoethylenic derivatives is left at this stage, and hence it is probable that the hydrogenation of squalene involves the simultaneous selective reduction of an original mixture of isomeric hexaolefinic hydrocarbons. This result tends to confirm the conclusions previously arrived at from a study of the squalene hexahydrochlorides (Part I).

As indicated by the curves, the selective nature of the hydrogenation process is very well marked. Whilst we have not at present

sufficient knowledge of the constitution of the products definitely to correlate each intermediate compound which may be formed with a break in the curve, it seems evident that the cause of the selectivity must reside in the varying degree of substitution of the ethylene groups. Lebedev, Koblianski, and Yakubchik (J., 1925, **127**, 417) have shown the extraordinary influence exerted by differences in the degree of substitution around a double bond upon the rate of hydrogenation; and we venture to suggest, from the generalisations of these authors, that our curves indicate that certainly three, and probably four, of the unsaturated centres in squalene exist at the moment of hydrogenation in the form $CH_2{:}C<$, which is merely an isomeric form of the structure suggested in a previous paper, for example,

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{:}CH\cdot CH_2\cdot[CH_2\cdot\overset{\displaystyle CH_2}{\overset{\|}{C}}\cdot CH_2\cdot CH_2]_4\cdot CH_2\cdot\overset{\displaystyle CH_3}{\overset{|}{C}}{:}CH\cdot CH_3.$$

This idea of the dissimilarity of two of the unsaturated linkings from the remaining four is stressed, not only by the marked difference in the rate of hydrogenation, but also by the fact that ring closure in squalene itself only proceeds to the stage at which four double bonds have disappeared.

Experiments have been carried out in the direction of ring closure of the partly hydrogenated products, and it has been definitely ascertained that, unlike squalene, those products which have been hydrogenated up to the point at which 3, 4, and 5 gram-molecules of hydrogen have been absorbed are wholly incapable of intramolecular condensation when boiled with 98% formic acid. The partial condensation noted in the case of the lesser-hydrogenated product containing four double bonds, as evidenced by the change in iodine value, may be due, at least in part, to a small amount of unchanged squalene, the presence of which we have established (compare below).

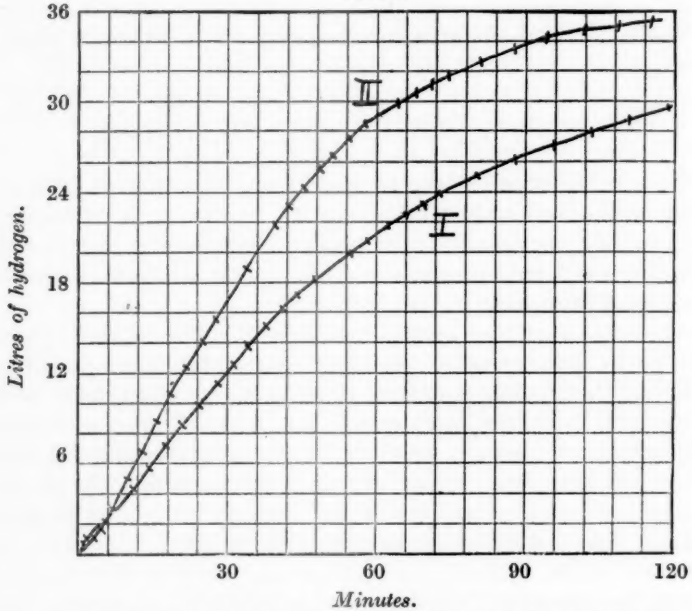
We have on several occasions observed that, contrary to general experience in hydrogenations of this type, the rate of absorption is relatively slow for a short period at the commencement of the reaction, but rapidly attains a maximum value. Whilst this phenomenon has not invariably been noted, its appearance with the nickel catalyst supported both on charcoal and on kieselguhr has been sufficiently frequent to justify us in recording it as an apparent example of an induction period (see curve I). Apart from this, the absorption–time relation is of the type most commonly encountered in cases of well-marked selective hydrogenation, the variations in rate of absorption over the whole course of hydrogenation covering a wide range. Thus, on the average, taking the rate of hydrogenation of the last ethenoid linking as unity, the relative speeds

for each double bond are represented approximately by the following figures:

Double bond	1	2	3	4	5	6
Rate	>10	<10	8	5·5	3	1

That the hydrogenation of squalene is indeed selective has been definitely established, since estimations of squalene by the hydrochloride method (see experimental part) have shown that after the absorption of 1 gram-molecule of hydrogen, 34% of squalene, and after the absorption of 2 gram-molecules only 1—2% of squalene,

FIG. 1.



I. 0·3 *G. of nickel on charcoal.* II. 0·3 *G. of nickel on kieselguhr.*

remain, and we have no doubt that if suitable methods of analysis could be devised, the same preponderance of one particular partly hydrogenated compound would be found at each intermediate stage.

As previously stated (Part I), squalene contains in many cases a minute quantity of an oxygenated product. We have now found that after hydrogenation a very small quantity of a crystalline compound (0·2%) separated from the cooled oil and could be completely removed by fractional distillation, the hydrogenated squalene being then entirely free from oxygen. The oxygenated compound is a neutral substance, m. p. 67—68°, which appears to be oxidic in character, as it forms neither an acetyl derivative, a semicarbazone, nor an oxime.

Experimental.

Hydrogenation of Squalene.—The hydrogenation was effected in a narrow, closed, cylindrical steel vessel of about 400 c.c. total capacity fitted with an efficient high-speed rotary stirrer, a thermometer pocket, a hydrogen inlet-tube extending nearly to the bottom of the vessel, and a gas exit-tube almost flush with the lid. The rate of stirring was as nearly as possible 2000 revs./min., and hydrogen from a cylinder was passed at a suitable rate through a meter into the hydrogenation apparatus, from which it emerged into a second meter after passing through a catchpot to trap any traces of liquid that might be splashed over. The flow of hydrogen was adjusted so that at the maximum rate of absorption about 20—25% of unabsorbed hydrogen was passing through the second meter. The meters were of the water type and measured 2·5 litres per revolution; they were checked together before each experiment and were also frequently calibrated directly by displacement of about 10 litres of water by hydrogen from an aspirator kept strictly under atmospheric pressure.

The temperature of the squalene during the measurements of rate of hydrogenation was 150° ± 2°. The catalyst employed was metallic nickel, mounted on kieselguhr or coconut charcoal; various concentrations of catalyst were employed in different experiments and typical results are shown, in the accompanying graphs, of the hydrogenation of 100 g. of squalene at 150° in the presence of 0·3 g. of nickel on coconut charcoal and on a kieselguhr support, respectively, with hydrogen flowing at 50—60 litres per hour and with constant stirring as described above.

At the conclusion of the process, the oil was filtered from nickel while still hot, and distilled under reduced pressure.

Products of Hydrogenation.—Dodecahydrosqualene. The completely hydrogenated product was a colourless, odourless, mobile oil, b. p. 222—226°/3 mm., 212—213°/1 mm.; $n_D^{20°}$ 1·4534; $d_{20°}^{20°}$ 0·8107; $[R_L]_D$ 140·9 (calc. for $C_{30}H_{62}$, 140·1) (Found: C, 85·5, 85·4; H, 14·8, 14·8. $C_{30}H_{62}$ requires C, 85·3; H, 14·7%).

Whereas squalene shows a remarkable exaltation of molecular refractivity ($\Sigma[R_L]_D = 2·1$) over the calculated value, this phenomenon completely disappears during hydrogenation.

In addition to the complete hydrogenation of squalene with simultaneous observation of the rate of absorption of hydrogen throughout the process, a number of experiments were subsequently undertaken in which the interaction was interrupted after 1, 2, 3, 4, or 5 g.-mols. of hydrogen per g.-mol. of squalene had been absorbed, and the partly hydrogenated products were examined.

1. *Absorption of* 1 *mol. of hydrogen.* The product had b. p. 235—238°/3 mm., $d_{20°}^{20°}$ 0·8534, and $n_D^{20°}$ 1·4872. On treatment with dry hydrogen chloride in ethereal solution, the oil (5 g.) yielded 1·7 g. of crystalline squalene hexahydrochloride (m. p. 112—118°). This is equivalent to 34% of unchanged squalene.

2. *Absorption of* 2 *mols. of hydrogen.* A colourless oil was obtained, b. p. 235—237°/3 mm., $n_D^{20°}$ 1·4800, $d_{20°}^{20°}$ 0·8443, iodine value 234·3 (calc. for $C_{30}H_{54}|^{=}_{4}$, 245). Absorption of dry hydrogen chloride yielded a quantity of squalene hexahydrochloride equivalent to 1·4% of squalene, together with an oil which could not be crystallised. Treatment of this hydrocarbon mixture with 98% formic acid for 15 hours yielded a partly cyclised product, b. p. 232—236°/4 mm., $n_D^{20°}$ 1·4900, iodine value 154·2.

3. *Absorption of* 3 *mols. of hydrogen.* The product was a colourless oil, b. p. 232—234°/3 mm., $n_D^{20°}$ 1·4710, $d_{20°}^{20°}$ 0·8334, iodine value 190 (calc. for $C_{30}H_{56}|^{=}_{3}$, 183). A crystalline hydrochloride could not be obtained by treatment with dry hydrogen chloride, and prolonged treatment with 98% formic acid produced no change.

4. *Absorption of* 4 *mols. of hydrogen.* The product had b. p. 229—234°/3 mm., $n_D^{20°}$ 1·4625, $d_{20°}^{20°}$ 0·8211, iodine value 124·5 (calc. for $C_{30}H_{58}|^{=}_{2}$, 121·4).

5. *Absorption of* 5 *mols. of hydrogen.* The principal hydrocarbon was obtained as a colourless, mobile oil, b. p. 228—231°/3 mm., $n_D^{20°}$ 1·4550, $d_{20°}^{20°}$ 0·8094, iodine value 64·8 (calc. for $C_{30}H_{60}|_{1}$, 60·4), which was recovered unchanged after prolonged treatment with formic acid.

In conclusion, we desire to thank the Council of the Department of Scientific and Industrial Research for a grant which enabled this work to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, November 2nd,* 1926.]

CCCCXXI.—*The Unsaponifiable Matter from the Oils of Elasmobranch Fish. Part III. Tetracyclosqualene and the Production of a New Naphthalene Hydrocarbon.*

By JOHN HARVEY, ISIDOR MORRIS HEILBRON, and EDWARD DAVID KAMM.

IT was shown by Heilbron, Kamm, and Owens (this vol., p. 1630) that the pyrogenic decomposition of squalene led to the formation, among other terpenes, of a complex sesquiterpene fraction from

which, on dehydrogenation with sulphur, a hydrocarbon was isolated which yielded a minute amount of a picrate, possibly cadalene picrate. As all attempts to obtain this compound in larger quantities have proved abortive, we have directed our attention to the tetracyclic isomeride derived from squalene in the hope of obtaining from it, by dehydrogenation, aromatic hydrocarbons in better yield. Whereas squalene itself reacts explosively with sulphur, the reaction with tetra*cyclo*squalene can be controlled and at 200—270° a vigorous evolution of gas occurs. Decomposition took place during the dehydrogenation, and from the mixed products were separated (*a*) a small quantity of a colourless, mobile oil resembling *m*- or *p*-cymene, and (*b*) a colourless oil, b. p. 100—160°/13 mm., which yielded a well-defined, crystalline picrate the analytical values for which agree with the formula $C_{19}H_{17}O_7N_3$. By decomposing this picrate with ammonia, a colourless, solid hydrocarbon (m. p. 33·5°) of formula $C_{13}H_{14}$ was obtained. This substance has a distinct naphthalene-like odour and its identity with a substituted naphthalene compound is suggested both by analogy with the dehydrogenation derivatives of typical sesquiterpenes (compare Ruzicka, *Helv. Chim. Acta*, 1922, **5**, 345) and by the abnormally high value of its molecular refractivity ($\Sigma[R_L]_D$ = 2·75), which is typical of all such hydrocarbons.

Of the numerous possible hydrocarbons of this formula, α- and β-propyl-, β-*iso*propyl-, and two trimethyl-naphthalenes have been described, but these differ from the compound under discussion.

As the yield of the hydrocarbon was extremely small, and as its formation appeared to be due to the preliminary decomposition of tetra*cyclo*squalene into less complex molecules, the destructive distillation of this compound was studied by the method already described for squalene itself. The complex mixture produced, which was in every way comparable with that obtained from squalene, was fractionated as previously described and a monoterpene fraction was obtained from which a portion closely resembling pinene in odour was isolated. This is being fully investigated.

The whole of the sesquiterpene fraction was treated with sulphur at 200—270° and thereafter the same hydrocarbon of m. p. 33·5° was isolated in 4% yield. Sufficient of this substance has not yet been obtained for the determination of its structure, but larger quantities are being collected for this purpose.

The diterpene fraction also was treated with sulphur, but the dehydrogenated products failed to give crystalline addition compounds with picric acid. This proves definitely that the picrate-forming aromatic hydrocarbon ($C_{13}H_{14}$) is produced from the sesquiterpene portions and hence almost confirms its naphthalene structure.

During the preparation of the comparatively large quantity of tetra*cyclo*squalene required in these experiments, squalene was upon one occasion treated with formic acid which had already been used once for the same purpose. The hydrocarbon produced, even after prolonged boiling with the reagent, differed in physical properties from normal tetra*cyclo*squalene, although it was undoubtedly also a tetracyclic substance. It showed the same exaltation of molecular refractivity and on treatment with sulphur yielded the same $C_{13}H_{14}$ hydrocarbon. It can only be assumed, therefore, that cyclisation in this case must have taken place in a different way, without, however, altering the carbon skeleton of the molecule or the positions of the two remaining ethenoid linkings to which the abnormal molecular refractivity has been ascribed.

EXPERIMENTAL.

*Dehydrogenation of Tetra*cyclo*squalene.* — Tetra*cyclo*squalene (200 g.) and finely-powdered sulphur (100 g.) were heated at 200—270° until, after 14 hours, evolution of hydrogen sulphide and mercaptan had ceased. The viscous, almost black product was separated by distillation into a deep red liquid (58 g.) and an unworkable resinous residue. The distillate was repeatedly distilled over bright metallic sodium until it was colourless and was then fractionated under reduced pressure, whereby the following fractions were obtained.

i. B. p. 70—75°/14 mm. (5 g.). A colourless oil with an odour indistinguishable from that of cymene. B. p. 170—180°/760 mm., $n_D^{20°}$ 1·5080, $d_{20°}^{20°}$ 0·8941. It still contained a trace of sulphur, probably in the combined state. The quantity at our disposal was insufficient for complete purification or further examination.

ii. B. p. 100—160°/13 mm. (25 g.). This portion consisted of a colourless oil giving no definite fractions on distillation. The whole was treated with a hot saturated alcoholic solution of picric acid, whereby gradual precipitation of an orange solid occurred; by treating the mother-liquor with more picric acid, further crops were obtained (total yield of crude substance, 4·3 g.). The picrate crystallised from absolute alcohol, in which it was only moderately easily soluble, in long, orange-red needles, m. p. 139—140° (Found: C, 56·8, 57·0; H, 4·3, 4·3; N, 10·7, 10·6. $C_{19}H_{17}O_7N_3$ requires C, 57·1; H, 4·3; N, 10·5%).

The Hydrocarbon $C_{13}H_{14}$.—The picrate was dissolved in ether and decomposed by warming under reflux with dilute aqueous ammonia. The ethereal solution was separated, washed with water, and dried. The colourless oil obtained from it was distilled at 15 mm., almost the whole coming over at 145° and solidifying on cooling. After crystallisation from hot 95% alcohol, it was obtained in centimetre-

long, colourless, silky needles, m. p. 33·5°. It is volatile in steam, only slightly soluble in cold methyl or ethyl alcohol, and readily soluble in ether and benzene: $d_{20°}^{20°}$ 1·0103, $n_D^{20°}$ 1·6110, $[R_L]_D$ 58·5 (calc. for $C_{13}H_{14}|_5^-$, 55·7) (Found: C, 91·6; H, 8·3. $C_{13}H_{14}$ requires C, 91·8; H, 8·2%).

The Destructive Distillation of Tetracyclosqualene.—Tetracyclosqualene (150 g.) was distilled under the conditions previously given for squalene itself (Heilbron, Kamm, and Owens, *loc. cit.*). The following groups of products were obtained.

	B. p.	Description.	Weight.
1	—	Combustible gas.	(1200 c.c./758 mm.)
2	28— 44°/758 mm.	Mobile, almost colourless oil.	2·5 g.
3	55—100°/20 mm.	Mobile, yellow oil.	44·0 ,,
4	110—180°/20 mm.	,, ,,	42·0 ,,
5	180—210°/20 mm.	Viscous ,,	11·5 ,,
6	210—280°/20 mm.	,, deep yellow oil.	10·0 ,,
7	—	Resinous residue.	25·0 ,,

Of these, groups 1, 2, 6, and 7 have not yet been examined; the liquid comprising group 2 has an odour identical with that of the amylene derived from squalene.

Group 3 was carefully refractionated from a Willstätter flask in a stream of nitrogen and again subdivided. By this means there was obtained a fraction (7·0 g.), b. p. 49—54°/15 mm. Refractionation of this at atmospheric pressure gave, as main portion, a liquid, b. p. 154—158°/758 mm., $d_{20°}^{20°}$ 0·8279, and $n_D^{20°}$ 1·4663. The odour closely resembled that of pinene.

Group 4 on refractionation was resolved into two main fractions: (*a*) b. p. 119—125°/14 mm., $d_{18°}^{18°}$ 0·8886, $n_D^{18°}$ 1·4940, $[R_L]_D$ 66·83; weight, 7·5 g.; (*b*) b. p. 138—158°/14 mm., $d_{18°}^{18°}$ 0·9111, $n_D^{18°}$ 1·5028, $[R_L]_D$ 66·16; weight, 15·0 g. ($[R_L]_D$ calc. for $C_{15}H_{24}|_2^-$, 66·1).

Each of these fractions was treated with sulphur as previously described, and the purified dehydrogenated product with alcoholic picric acid. From each the picrate, m. p. 139—140°, was isolated. The total yield of the hydrocarbon $C_{13}H_{14}$ given by this method is no better than that obtained from tetracyclosqualene itself, the only advantage of the method being that the monoterpene and diterpene fractions are preserved.

Group 5, which was obviously composed of diterpenes, was treated as a whole with sulphur, but failed to yield a dehydrogenation product that would form a solid picrate.

Preparation of an Isomeric Tetracyclosqualene.—On one occasion, for reasons of economy, squalene was caused to cyclise by the use of formic acid which had previously been employed for the same purpose. A comparatively mobile liquid was obtained which could not be further changed by treatment with fresh formic acid: b. p.

228—230°/3 mm., $d_{20°}^{20°}$ 0·9237, $n_D^{20°}$ 1·5098, $[R_L]_D$ 132·7, iodine value 111·3 (calc. for $C_{30}H_{50}|_2^=$, 124).

On treatment of this new compound (245 g.) with sulphur (140 g.) at 200—280° as described above, 56 g. of volatile products were obtained. These were fractionated into (1) b. p. 70—120°/15 mm., (2) b. p. 120—165°/15 mm., and (3) b. p. 165—185°/15 mm. On treatment of these fractions with alcoholic picric acid, No. 2 readily yielded 4 g. of a picrate, m. p. 139—140°, identical with that already obtained from the compound $C_{13}H_{14}$.

In conclusion, we desire to record our thanks to the Department of Scientific and Industrial Research for grants which enabled this work to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, November 2nd*, 1926.]

CCCCXXII.—*Derivatives of Acenaphthpyridine. Part I.*

By SRIKUMARAN UNNI NAIR and JOHN LIONEL SIMONSEN.

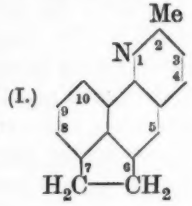
DURING an investigation of derivatives of naphthaquinoline (this vol., p. 2247) it was observed that, whilst α-naphthylamine itself could not be condensed with paraldehyde, its derivatives substituted in the 4-position readily underwent this reaction. In order to ascertain whether 4-substitution was the determining factor, we decided to examine the condensation of 5-aminoacenaphthene with paraldehyde, since this base may be regarded as a derivative of α-naphthylamine in which the 4-position is substituted.

Cyclic nitrogen derivatives containing the acenaphthene nucleus have been little investigated and it was only when this work was nearing completion that a paper appeared (Stewart, J., 1925, **127**, 1331) in which an account was given of the preparation of acenaphthpyridine.*

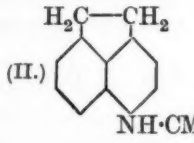
When digested with hydrochloric acid, 5-aminoacenaphthene and paraldehyde readily condense with formation of *2-methylacenaphthpyridine* (I), thus confirming the suggestion that substitution in position 4 is the deciding factor in this reaction. On reduction with sodium and alcohol, 2-methylacenaphthpyridine is converted into the corresponding *tetrahydro-base*, but the yield is poor owing to the simultaneous production of more highly reduced bases. No better results were obtained by using other reducing agents.

* The name acenaphthpyridine appears to the authors to be preferable to that of α-acenaphthaquinoline, since the latter name should really be given to a substance containing both the acenaphthene and the quinoline ring.

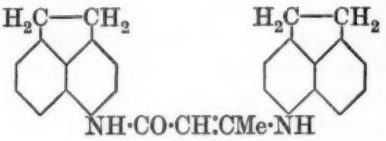
The condensation of 5-aminoacenaphthene with ethyl acetoacetate proceeds like that of α- and β-naphthylamines. A description of the products is given below.



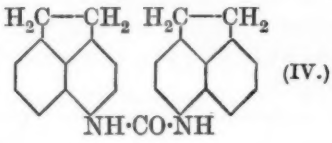
(I.)



(II.)



(III.)



(IV.)

EXPERIMENTAL.

Condensation of 5-Aminoacenaphthene and Paraldehyde. 2-*Methylacenaphthpyridine* (I).—A mixture of 5-aminoacenaphthene (10 g.), hydrochloric acid (*d* 1·19; 20 g.), and paraldehyde (15 g.) developed an intense red colour at 50°, a vigorous reaction took place at 70°, and after 15 minutes the condensation was completed by heating at 110° for 5 hours. An excess of alkali was added, the semi-solid, viscid brown oil that separated was dissolved in dilute sulphuric acid and treated with a slight excess of sodium nitrite solution to remove the secondary base which had been formed, and the filtered solution was made alkaline with ammonia. The base (6 g.) obtained was crystallised from dilute alcohol. 2-*Methylacenaphthpyridine* separated from alcohol in irregular, colourless prisms, m. p. 131°, which became brown somewhat rapidly on exposure to air. It was readily soluble in the ordinary organic solvents except light petroleum (Found: C, 87·6; H, 6·1; N, 6·7. $C_{16}H_{13}N$ requires C, 87·7; H, 5·9; N, 6·4%).

The *hydrochloride* and *hydrobromide* were somewhat sparingly soluble in water and crystallised in needles. The *picrate* separated from alcohol in glistening, yellow prisms, decomp. 225—226° (Found: N, 12·9. $C_{22}H_{16}O_6N_4$ requires N, 13·0%). The *chloroplatinate*, which was insoluble in water and alcohol, was deposited on the addition of platinic chloride to a solution of the hydrochloride as a brown, crystalline powder, decomp. 251—252° (Found: Pt, 23·1. $C_{32}H_{28}N_2Cl_6Pt$ requires Pt, 23·0%).

2-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacenaphthpyridine.*—A solution of 2-methylacenaphthpyridine (10 g.) in boiling alcohol (600 c.c.) was

treated with sodium (40 g.), the alcohol then removed in steam, and the *tetrahydro-base* separated by ether. It distilled at 215—217°/14 mm.; the distillate, which slowly crystallised, separated from alcohol in glistening prisms, m. p. 88—89° (Found: C, 85·9; H, 7·9; N, 6·5. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6; N, 6·3%). The base, which was readily soluble in all the ordinary organic media except alcohol, gave strongly fluorescent solutions which darkened rapidly on exposure to the air. The yield of tetrahydro-base was very poor, a considerable quantity of liquid bases of lower boiling point being formed simultaneously. When other reducing agents such as sodium amalgam, tin and hydrochloric acid, and amalgamated zinc and hydrochloric acid were used, the original base was recovered unchanged.

The *hydrochloride* separated from dilute alcohol in ill-defined crystals, decomp. 260—261° (Found: Cl, 13·8. $C_{16}H_{17}N,HCl$ requires Cl, 13·7%). The *benzoyl* derivative crystallised from alcohol in rectangular plates, m. p. 187—188° (Found: C, 84·1; H, 6·8. $C_{23}H_{21}ON$ requires C, 84·4; H, 6·4%).

Condensation of 5-Aminoacenaphthene and Ethyl Acetoacetate.—(i) *Ethyl β-5-acenaphthylaminocrotonate* (II). To a mixture of 5-aminoacenaphthene (9 g.), ethyl acetoacetate (7 g.), and sufficient alcohol to give a clear solution, piperidine (2 drops) was added. After 12 hours, the crystalline solid was collected; it recrystallised from alcohol in plates, m. p. 83—84°. The *ester* was readily soluble in the ordinary organic solvents (Found: C, 76·9; H, 6·9; N, 5·3. $C_{18}H_{19}O_2N$ requires C, 76·9; H, 6·8; N, 5·0%).

4-Hydroxy-2-methylacenaphthpyridine, obtained in a quantitative yield when ethyl β-5-acenaphthylaminocrotonate was heated to 220°, crystallised from acetic acid in thin, glistening plates, m. p. above 330°. It was insoluble in all the ordinary solvents except acetic acid and nitrobenzene, showed very feeble basic properties, and gave no colour with ferric chloride (Found: C, 81·5; H, 5·6; N, 6·0. $C_{16}H_{13}ON$ requires C, 81·7; H, 5·5; N, 6·0%).

(ii) *β-5-Acenaphthylaminocroton-5-acenaphthylamide* (III).—A mixture of 5-aminoacenaphthene (23 g.) and ethyl acetoacetate (18 g.) was heated on the water-bath for 8 hours, a further equal quantity of ethyl acetoacetate then added, and the heating continued for 5 hours at 170°. The cooled solid residue was powdered, thoroughly washed with alcohol, and crystallised from toluene, which left undissolved a small quantity of a substance (*A*).

β-5-Acenaphthylaminocroton-5-acenaphthylamide crystallised in rosettes of needles, m. p. 189—190°. It was insoluble in water, somewhat readily soluble in acetic acid, ethyl acetate, acetone, or pyridine, and more sparingly soluble in benzene or chloroform

(Found: C, 83·2; H, 6·2; N, 7·1. $C_{28}H_{24}ON_2$ requires C, 83·2 H, 5·9; N, 6·9%).

5-Acetoacetamidoacenaphthene.—The crotonamide (III) (20 g.) was mixed with hydrochloric acid (320 c.c. of 4%) and heated on the water-bath for 15 minutes. The solid product, after being washed with boiling water to remove 5-aminoacenaphthene hydrochloride, crystallised from dilute alcohol in fine needles, m. p. 142—143° (Found: C, 76·0; H, 6·2; N, 5·9. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9; N, 5·5%).

2-Hydroxy-4-methylacenaphthpyridine.—A mixture of 5-acetoacetamidoacenaphthene (11 g.) and concentrated hydrochloric acid (10 c.c.) was heated on the water-bath for 10 minutes; the solid that separated on pouring the product into water was repeatedly extracted with boiling water to remove 5-aminoacenaphthene hydrochloride formed by hydrolysis. The *hydroxy-base* crystallised from nitrobenzene in glistening prisms, m. p. above 350°. It was extremely sparingly soluble in the ordinary solvents and gave no colour with ferric chloride (Found: C, 82·0; H, 5·8; N, 6·3. $C_{16}H_{13}ON$ requires C, 81·7; H, 5·5; N, 6·0%). A solution in hot hydrochloric acid, on cooling, deposited a sparingly soluble *hydrochloride* which was readily dissociated by water.

2-Chloro-4-methylacenaphthpyridine.—A suspension of the hydroxy-base (0·6 g.) and phosphorus pentachloride (1 g.) in phosphorus oxychloride (10 c.c.) was heated at 107° for 3 hours. After addition of ice, the *chloro*-compound was collected; it crystallised from alcohol in needles, m. p. 200—201°. It was readily soluble in benzene, chloroform, or acetic acid, somewhat sparingly soluble in alcohol, and insoluble in light petroleum (Found: N, 5·6; Cl, 14·0. $C_{16}H_{12}NCl$ requires N, 5·5; Cl, 14·0%).

4-Methyl-1 : 2 : 3 : 4-tetrahydroacenaphthpyridine was obtained by reducing the above chloro-derivative with sodium and alcohol. After purification through the sparingly soluble *hydrobromide*, it crystallised from alcohol in fine needles, m. p. 87—88° (Found: C, 85·9; H, 7·8. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6%).

s-Di-5-acenaphthylcarbamide (IV).—The substance (*A*) (see p. 3142) which was insoluble in toluene crystallised from much nitrobenzene in prismatic needles, m.p. 318°. It was identified as the substituted carbamide by direct comparison with a specimen prepared by heating a mixture of urea and 5-aminoacenaphthene at 200° for 2 hours (Found: C, 82·5, 82·1*; H, 5·6, 5·5*; N, 8·4. $C_{25}H_{20}ON_2$ requires C, 82·4; H, 5·5; N, 7·7%).

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[*Received, November 1st*, 1926.]

* Specimen prepared from urea.

CCCCXXIII.—3-*Methoxy*-2-*phenylindole* and 3-*Benzoylamino*-2-*phenylindole*.

By ROBERT ROBINSON and SIDNEY THORNLEY.

THE substances mentioned in the title have been prepared in order to show that E. Fischer's method can be extended to the synthesis of indole derivatives in which an oxygen or a nitrogen atom is directly attached to the pyrrole nucleus.

3-*Methoxy*-2-*phenylindole*, $C_6H_4<\begin{matrix}C(OMe)\\NH\end{matrix}>CPh$.—A mixture of ω-methoxyacetophenone (10 g.) (Pratt and Robinson, J., 1923, **123**, 748; compare Malkin and Robinson, J., 1925, **127**, 372) and phenylhydrazine (10·7 g.) became warm and when the initial reaction ceased the formation of the phenylhydrazone was completed by heating on the steam-bath for 5 minutes. Acetic acid (100 c.c.) was then introduced and the yellow solution heated; it gradually became redder and at a certain stage a strong exothermic reaction occurred and the liquid boiled spontaneously. The crimson solution was then boiled for 40 minutes, cooled, and added to much water. The oil quickly crystallised; it was dried and repeatedly extracted with boiling petroleum (b. p. 80—100°), the yellowish-brown material which crystallised from the filtered solutions weighing 9·5 g. On recrystallisation from the same solvent, almost colourless prisms, m. p. 106°, were obtained (Found: C, 80·7; H, 5·8; N, 6·4. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·8; N, 6·3%).

3-*Methoxy*-2-*phenylindole* is readily soluble in the usual organic solvents with the exception of light petroleum; it separates from aqueous alcohol in leaflets. The substance is somewhat sensitive to acids and its conversion into phenylindoxyl has not been accomplished smoothly. The action of a boiling mixture of phenol and hydrobromic acid (*d* 1·7) gave rise to products having the reactions of phenylindoxyl and of 2-phenylindolone—2-phenylindoxyl (Kalb and Bayer, *Ber.*, 1912, **45**, 2150), but these could not be fully purified.

Reduction by hydriodic acid. A mixture of methoxyphenylindole (3 g.), phenol (30 g.), and hydriodic acid (20 c.c.; *d* 1·7) was boiled for 1¼ hours. After cooling, addition of water and sodium hydroxide, isolation of the solid precipitate, and crystallisation from petroleum, 0·7 g. of the crude material was obtained. The substance was identified as 2-phenylindole and after crystallisation from alcohol had m. p. 186°, alone or mixed with a specimen prepared as described by Fischer (*Annalen*, 1886, **236**, 133).

3-*Benzoylamino*-2-*phenylindole*, $C_6H_4<\begin{matrix}C(NHBz)\\NH\end{matrix}>CPh$.—ω-Benzoylaminoacetophenone (Robinson, J., 1909, **95**, 2167; Gabriel,

Ber., 1910, **43**, 134) forms a *phenylhydrazone* which crystallises from alcohol in stout, colourless needles, m. p. 153° (Found : N, 12·7. $C_{21}H_{19}ON_3$ requires N, 12·8%). The indole derivative was normally obtained without isolating this intermediate. A mixture of ω-benzoylaminoacetophenone (22 g.) with phenylhydrazine (23 g.) was heated on the steam-bath for ½ hour, and acetic acid (220 c.c.) then introduced. The orange liquid was heated over gauze; it became crimson and a vigorous reaction ensued; finally, the solution was boiled for 1 hour. The yellow, viscous mass obtained on the addition of water soon hardened and was collected, dried, and crystallised from toluene. The total yield, including a portion recovered from the mother-liquor by concentration and addition of light petroleum, amounted to 12 g. The substance crystallises from toluene in tablets, m. p. 206°. In another experiment, the dried crude product was twice extracted with a mixture of equal volumes of benzene and light petroleum; the residue crystallised from aqueous alcohol in silvery leaflets, m. p. 201·5° (Found : C, 80·8; H, 5·2; N, 8·9. $C_{21}H_{16}ON_2$ requires C, 80·8; H, 5·1; N, 9·0%). The melting point of a mixture of the tablets and leaflets was 206°. The substance is readily soluble in ethyl alcohol, acetone or acetic acid, moderately readily soluble in methyl alcohol, ethyl acetate, toluene, or xylene, less soluble in benzene or chloroform, and sparingly soluble in light petroleum.

Numerous attempts were made to hydrolyse this amide under the most varied conditions, but in no case could the process be smoothly accomplished. Benzoylaminophenylindole (0·5 g.) mixed with ethyl alcohol (10 c.c.) and concentrated hydrochloric acid (10 c.c.) was heated in a sealed tube at 125—130° for 4 hours. Water was added, unchanged material removed by extraction with ether, and the aqueous layer basified; the precipitated solid, crystallised from benzene, had m. p. 171·5°. Furthermore, in an attempt to prepare a derivative of 6-carboline by intramolecular condensation, a mixture of benzoylaminophenylindole (0·5 g.) and an excess of phosphorus trichloride was boiled for 5 minutes. After treatment with water, filtration, and basification, a substance was isolated which was crystallised from benzene–petroleum. This had m. p. 174° and a mixture with the specimen, m. p. 171·5°, had m. p. 172° (Found : N, 13·5, 13·2. Calc. for $C_{14}H_{12}N_2$: N, 13·4%). Fischer and Schmitt (*Ber.*, 1888, **21**, 1074) prepared 3-amino-2-phenylindole by reducing 3-nitroso-2-phenylindole and state that it has m. p. 174°.

THE UNIVERSITY, MANCHESTER. [*Received, November* 13*th*, 1926.]

CCCCXXIV.—*The Partial Esterification of Polyhydric Alcohols. Part IV. The Oxidation of Allyl Esters to α-Monoglycerides.*

By ARTHUR FAIRBOURNE and GRAHAM EDWARD FOSTER.

ALLYL alcohol and its homologues have been oxidised to the corresponding glycerols by potassium permanganate (Wagner, *Ber.*, 1888, **21**, 1231, 3351; 1890, **23**, 2313), and sodium chlorate solution, activated by a trace of osmium tetroxide (Hofmann, *Ber.*, 1912, **45**, 3335; Hofmann, Ehrhart, and Schneider, *Ber.*, 1913, **46**, 1657), has also been used in similar reactions. The nearest approach to the direct oxidation of an allyl ester to an α-monoglyceride

$$CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}COX \xrightarrow{H_2O + O_2} OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}COX$$

so far recorded, however, is Bailly's synthesis of α-monoglycerophosphoric acid from allylphosphoric acid (*Compt. rend.*, 1915, **160**, 663).

The failure of the previous attempts (J., 1921, **119**, 1038) to oxidise allyl esters directly to α-monoglycerides has now been traced to the difficulty of finding a suitable solvent, allyl esters being practically insoluble in water and most organic solvents being themselves attacked by oxidising agents of the kind required.

Allyl *p*-nitrobenzoate and 3 : 5-dinitrobenzoate have been oxidised, by suitably treating solutions in acetone with aqueous potassium permanganate, to the corresponding α-monoglycerides, which have been proved identical with authentic specimens prepared from *iso*propylidene glycerol (Fischer, *Ber.*, 1920, **53**, 1596) or monosodium glyceroxide (J., 1925, **127**, 2759). Glycerol α-2 : 4-dinitrophenyl ether (*loc. cit.*, J., 1921) also has been obtained by oxidising allyl 2 : 4-dinitrophenyl ether. The yields are not good, but the method is capable of producing α-monoglycerides of a high degree of purity.

Aqueous sodium chlorate activated by osmium tetroxide (Hofmann, Ehrhart, and Schneider, *loc. cit.*), and also hydrogen peroxide, were unsuccessfully tried as oxidising agents; the latter had no action on the allyl esters in acetone solution, and the former oxidised them apparently to compounds other than glycerides.

Allyl picrate (allyl 2 : 4 : 6-trinitrophenyl ether) resisted oxidation to the corresponding glyceride and attempts to prepare this substance from monosodium glyceroxide and from α-monochlorohydrin failed.

The allyl esters prepared during this investigation were characterised each by the preparation of the dibromo-derivative.

EXPERIMENTAL.

Allyl p-*Nitrobenzoate.*—4 G. of quinoline were added to 5·6 g. of *p*-nitrobenzoyl chloride, the product was dissolved in 10—15 c.c. of chloroform, 2 c.c. of allyl alcohol were added, and the whole was kept for 2 days. Ether was then added in excess and the mixture was shaken with water, dilute sulphuric acid, sodium bicarbonate solution, and again with water. After the ethereal solution had been dried with fused sodium sulphate, the solvent was removed; the residual oil solidified on cooling and crystallised from alcohol in needles, m. p. 30° (yield, 4·3 g.) (Found: C, 58·5; H, 4·4. Calc.: C, 58·0; H, 4·35%). This compound has been described as an oil (A.P. 1360994) and as a solid of m. p. 28° (Meisenheimer, *Ber.*, 1919, **52**, 1675).

Dibromo-derivative. Allyl *p*-nitrobenzoate and bromine in slight excess were kept in chloroform. After ½ hour, the solvent was removed, and the excess of bromine volatilised on a water-bath; the oily residue, which solidified, crystallised from alcohol in plates, m. p. 57—58° (yield, nearly theoretical) (Found: Br, 43·7. $C_{10}H_9O_4NBr_2$ requires Br, 43·6%).

Oxidation of Allyl p-*Nitrobenzoate to Glycerol* α-*Mono*-p-*nitrobenzoate.*—A solution of 0·5 g. of allyl *p*-nitrobenzoate in 100 c.c. of acetone was treated with 79 c.c. of 1% aqueous potassium permanganate. After some hours, the manganese dioxide was removed, the filtrate neutralised with dilute hydrochloric acid, the acetone distilled off, and the residue evaporated to 40—50 c.c. on a water-bath. The hot filtered solution deposited over-night 0·25 g. of pure, crystalline glycerol α-mono-*p*-nitrobenzoate which, alone or mixed with authentic specimens prepared from monosodium glyceroxide or *iso*propylidene glycerol (J., 1925, **127**, 2763), melted at 107°.

Allyl 3 : 5-*dinitrobenzoate* was prepared, in the same way as the *p*-nitrobenzoate, from 4 g. of quinoline, 6·6 g. of 3 : 5-dinitrobenzoyl chloride in 15 c.c. of dry chloroform, and 2 c.c. of allyl alcohol. The crude product (5·4 g.), on crystallisation from alcohol, yielded long needles, m. p. 50° (compare A. P. 1360994) (Found: C, 47·6; H, 3·5. Calc.: C, 47·6; H, 3·2%).

The *dibromo*-derivative, prepared in the same way as the preceding one (yield, theoretical), crystallised from alcohol in plates, m. p. 85° (Found: Br, 38·5. $C_{10}H_8O_6N_2Br_2$ requires Br, 38·8%).

Oxidation of Allyl 3 : 5-*Dinitrobenzoate to Glycerol* α-*Mono*-3 : 5-*dinitrobenzoate.*—The glyceride was prepared (65 c.c. of 1% aqueous potassium permanganate were used) and isolated in the same way as the *p*-nitrobenzoate. The product, after being dried in a vacuum over sulphuric acid, crystallised from chloroform in needles which, alone or mixed with an authentic specimen (J., 1925, **127**,

2763), melted at 118°. The yield was 0·25 g. from 0·5 g. of allyl 3 : 5-dinitrobenzoate.

Oxidation of Allyl 2 : 4-*Dinitrophenyl Ether to Glycerol* α-*Mono*-2 : 4-*dinitrophenyl Ether.*—A solution of 0·96 g. of allyl 2 : 4-dinitrophenyl ether (J., 1921, **119**, 1038) in 130 c.c. of acetone was treated with the equivalent quantity of 1% aqueous potassium permanganate and kept for 12 hours. The glycerol ether was isolated as in the other cases, but the final solution was evaporated to 100 c.c. before being left over-night to crystallise. The product was dried in a vacuum over sulphuric acid and recrystallised from benzene; it then melted at 85°, alone or mixed with an authentic specimen of glycerol α-mono-2 : 4-dinitrophenyl ether (*ibid.*, p. 1037). The yield was 20—30%.

Allyl 2 : 4 : 6-*Trinitrophenyl Ether.*—Picryl chloride (4·9 g.), dissolved in 25 c.c. of allyl alcohol, was added to a cold solution of 1·14 g. of potassium hydroxide in the same solvent (10 c.c.). After ½ hour, the mixture was warmed and poured into 200 c.c. of water; the *ether* then separated. It crystallised from alcohol in long needles (yield, 2—3 g.), m. p. 90° (Found : N, 15·75. $C_9H_7O_7N_3$ requires N, 15·6%).

This reaction is erratic and the yield stated is the best obtained. In some experiments, no ether was produced, potassium picrate being the only substance isolated.

The *dibromo*-derivative was prepared and isolated as in the other two cases. It crystallised from alcohol in prisms, m. p. 106—107° (yield, theoretical) (Found : Br, 37·9. $C_9H_7O_7N_3Br_2$ requires Br, 37·3%).

The authors wish to thank the Department of Scientific and Industrial Research for a maintenance grant which enabled one of them to take part in this investigation.

KING'S COLLEGE, LONDON, W.C. 2. [*Received, October 4th*, 1926.]

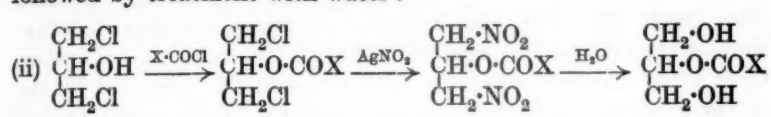
CCCCXXV.—*The Partial Esterification of Polyhydric Alcohols. Part V. The α-Structure of Alleged "β"-Monoglycerides.*

By ARTHUR FAIRBOURNE and GRAHAM EDWARD FOSTER.

GRÜN (*Ber.*, 1910, **43**, 1288) proposed the reaction between β-monochlorohydrin and the potassium salts of acids for the preparation of β-monoglycerides,

(i) $OH\cdot CH_2\cdot CHCl\cdot CH_2\cdot OH \xrightarrow{X\cdot CO_2K} OH\cdot CH_2\cdot CH(O\cdot COX)\cdot CH_2\cdot OH,$

and claimed to have produced these compounds independently by the reaction between esters of αγ-dichlorohydrin and silver nitrite, followed by treatment with water :



Both these methods have now been examined : the latter gives α-compounds (compare Gilchrist and Purves, J., 1925, **127**, 2735, who, when endeavouring to prepare β-methyl glycerol, obtained the α-compound instead) and the former depends on an untrustworthy initial material.

The possibility of β-substitution in the glycerol molecule was first confirmed by proving that the *p*-nitrobenzoates of αγ- and αβ-dibromohydrins are not identical (compare, however, Fischer, *Ber.*, 1920, **53**, 1621, and Gilchrist and Purves, *loc. cit.*, who obtained αγ-derivatives when they expected to obtain αβ).

The preparation of the alleged " β "-monoglycerides from β-monochlorohydrin (Grün's first method) was next investigated. The instructions of Hanriot (*Ann. Chim. Phys.*, 1879, **17**, 76) were followed and a constant-boiling specimen of " β "-monochlorohydrin was obtained which had physical constants very similar to those of the α-compound. It was therefore converted into its di-*p*-nitrobenzoate. This differed from the di-*p*-nitrobenzoate of α-monochlorohydrin only in melting a few degrees lower. The depression was caused by an impurity, which could be removed by recrystallisation and was shown, by analysis of the crude mixture, to have the composition of a monochlorohydrin di-*p*-nitrobenzoate. The " β "-monochlorohydrin is, therefore, a mixture of α- and β-monochlorohydrins (compare Smith, *Z. physikal. Chem.*, 1918, **92**, 717) and no monoglyceride of undoubted structure can be obtained from it by Grün's first method of synthesis (compare Thieme, *J. pr. Chem.*, 1912, **85**, 284; Lipp and Miller, *ibid.*, 1913, **88**, 361, regarding the untrustworthy nature of the reactions between glycerol chlorohydrins and the potassium salts of acids).

For the examination of Grün's second method for synthesising " β "-monoglycerides the *p*-nitrobenzoate and 3 : 5-dinitrobenzoate of αγ-dichlorohydrin were first prepared. They, however, and also αγ-dibromohydrin *p*-nitrobenzoate, did not react with silver nitrite to yield monoglycerides, and thus the statement was confirmed (Grün, *loc. cit.*) that the synthesis fails with esters of such acids as benzoic or acetic acid.

Finally, Grün's actual synthesis (*loc. cit.*) was repeated, in which the laurate of αγ-dichlorohydrin was heated with silver nitrite. The

alleged "β"-monolaurin was isolated from the product, and its melting point confirmed. Pure α-monolaurin of undoubted structure was prepared from *iso*propylidene glycerol by Fischer's method (*Ber.*, 1920, **53**, 1600), and a mixed melting-point determination showed that it was identical with the "β"-monolaurin. Further, Grün's "β"-monopalmitin (*loc. cit.*) was similarly prepared by the action of silver nitrite on palmityl αγ-dichlorohydrin and proved identical with the α-compound prepared from *iso*propylidene glycerol (Fischer, *loc. cit.*, p. 1604).

Experimental.

*Glycerol α-Monochlorohydrin Di-*p*-nitrobenzoate.*—A mixture of α-monochlorohydrin (b. p. 135°/32 mm.; supplied by British Drug Houses) (2·2 g.) and 5·6 g. of quinoline was dissolved in 5 c.c. of dry chloroform, and 7·48 g. of *p*-nitrobenzoyl chloride, dissolved in 10—15 c.c. of dry chloroform, were added slowly with cooling. After 24 hours, ether was added and the mixture was shaken with water, dilute sulphuric acid, sodium bicarbonate solution, and again with water. The ethereal extract was dried over fused sodium sulphate, and the solvent removed. The residual oil (yield, quantitative) solidified and was then washed with alcohol and acetone and crystallised from ligroin–acetone, needles, m. p. 107—108°, being obtained (Found: C, 50·5; H, 3·6. $C_{17}H_{13}O_8N_2Cl$ requires C, 49·95; H, 3·2%).

"Glycerol β-monochlorohydrin di-*p*-nitrobenzoate" was prepared in exactly the same way from the alleged β-monochlorohydrin obtained by Hanriot's method (*loc. cit.*). The di-*p*-nitrobenzoate crystallised from ligroin–acetone in needles resembling those described above but melting indefinitely at 100—104°. (A mixture of the two specimens melted at a slightly higher temperature.) After several recrystallisations from ligroin–acetone, however, α-monochlorohydrin di-*p*-nitrobenzoate was obtained which, alone or mixed with an authentic specimen, melted at 107—108°.

The impurity in the crude product of m. p. 100—104° was proved to be an isomeride by analysis of the latter (Found: C, 50·4; H, 3·5. Calc.: C, 49·95; H, 3·2%). By continued fractional crystallisation, a substance, m. p. 121—122°, was isolated; this lowered the m. p. of α-monochlorohydrin di-*p*-nitrobenzoate and was probably the true β-isomeride, but the quantity obtained was too small for accurate analysis (Found: C, 51·8; H, 3·8%).

Glycerol αγ-Dichlorohydrin p-*Nitrobenzoate* (compare Conant and Quayle, *J. Amer. Chem. Soc.*, 1923, **45**, 2771).—αγ-Dichlorohydrin (b. p. 175—177°; 5·16 g.) was treated with quinoline (5·6 g.) and *p*-nitrobenzoyl chloride (7·48 g.) in dry chloroform (15—20 c.c.);

the ester, isolated from the product in the usual manner, was quite pure and melted at 59—60° (yield, quantitative).

Glycerol αγ-dichlorohydrin 3 : 5-*dinitrobenzoate* was prepared by the same method, 8·8 g. of 3 : 5-dinitrobenzoyl chloride being used in place of *p*-nitrobenzoyl chloride. The product crystallised from alcohol in needles, m. p. 129° (yield, quantitative) (Found : Cl, 21·5. $C_{10}H_8O_6N_2Cl_2$ requires Cl, 22·0%).

Glycerol αγ-dibromohydrin p-*nitrobenzoate* was obtained in almost quantitative yield from 4·58 g. of αγ-dibromohydrin (Aschan, *Ber.*, 1888, **21**, 2890), 3·93 g. of *p*-nitrobenzoyl chloride, 3 g. of quinoline, and 15 c.c. of dry chloroform. It crystallised from alcohol in needles, m. p. 77—78° (Found : C, 33·0; H, 2·7. $C_{10}H_9O_4NBr_2$ requires C, 32·7; H, 2·5%). This compound is obviously not identical with the *p*-nitrobenzoate of αβ-dibromohydrin (preceding paper).

Preparation of the Alleged "β"-*Monolaurin.*—This compound was prepared by Grün's method (*Ber.*, 1910, **43**, 1289). The lauryl αγ-dichlorohydrin obtained boiled at 155—160°/1 mm. and the "β"-monolaurin melted at 61·5—62°. The lauryl αγ-dichlorohydrin was alternatively prepared by the method described above for the *p*-nitrobenzoate. It then occurred as a solid, m. p. 3°.

Preparation of α-Monolaurin.—This compound was prepared from *iso*propylidene glycerol by Fischer's method (*Ber.*, 1920, **53**, 1600). The lauryl *iso*propylidene glycerol obtained, b. p. 155—156°/1 mm., was hydrolysed to α-monolaurin by cold hydrochloric acid in the way he described (*loc. cit.*). After recrystallisation from ether–ligroin solution this melted at 62°, and at 61·5—62° when mixed with the alleged "β"-monolaurin (m. p. 61·5—62°).

Preparation of the Alleged "β"-*Monopalmitin.*—This compound was also prepared by Grün's method (*ibid.*, 1290). The palmityl αγ-dichlorohydrin crystallised from alcohol, m. p. 34° (compare Whitby, this vol., p. 1460), and the "β"-monopalmitin melted at 74—75°.

Preparation of α-Monopalmitin.—This compound was prepared from *iso*propylidene glycerol by the method of Fischer (*loc. cit.*, p. 1604), and crystallised from ligroin (b. p. 60—80°) in plates which melted at 74—75° alone or mixed with the alleged "β" monopalmitin.

The authors wish to express their indebtedness to the Chemical Society for a grant which has partly defrayed expenses incurred in this work, and also to the Department of Scientific and Industrial Research for a maintenance grant which enabled one of them to take part in it.

KING'S COLLEGE, LONDON, W.C. 2. [*Received, October 4th*, 1926.]

CCCCXXVI.—*The Absolute Density and Coefficient of Expansion of Silicon Tetrachloride.*

By PERCY LUCOCK ROBINSON and HAROLD CECIL SMITH.

IT has been already reported (*Nature*, 1926, **118**, 303) that the densities and coefficients of thermal expansion of silicon tetrachloride previously given by us (this vol., p. 1262) were relative, the difference in density of the glass floats at the temperature of standardisation and of use not having been considered. The makers of Durosil glass give $14{\cdot}1 \times 10^{-6}$ as the coefficient of cubical expansion. Prof. W. E. S. Turner, to whom we applied for information, very kindly calculated the probable value from its composition and obtained 15×10^{-6}. We have since made a rough measurement by a flotation method and our results indicate that the second value is probably nearer to the truth. If corrections based on this figure are applied to the data in Table VIII (*loc. cit.*, p. 1279) the new values of the absolute density are as set out in Table I, in which for the sake of comparison the previous relative results also are incorporated. Table II gives the coefficients of thermal expansion derived from these new values.

TABLE I.

Source.	Relative d at 20·00°.	Diff. from mean ($\times 10^6$).	Absolute d at 20·00°.	Diff. from mean ($\times 10^6$).
Canada	1·481231	−14	1·481461	−14
U.S.A.	1·481230	−15	1·481461	−14
Sweden	1·481223	−22	1·481454	−21
Scotland	1·481266	+21	1·481496	+21
France.....	1·481273	+28	1·481503	+28
Mean	1·481245	±20	1·481475	±20

TABLE II.

Source.	Relative coeff. of expansion.	Diff. from mean ($\times 10^7$).	Absolute coeff. of expansion.	Diff from mean ($\times 10^7$).
Canada	0·0014163	+39	0·0014082	+38
U.S.A.	0·0014109	−15	0·0014029	−15
Sweden	0·0014136	+12	0·0014056	+12
Scotland	0·0014083	−41	0·0014005	−39
France.....	0·0014129	+ 5	0·0014047	+ 3
Mean	0·0014124	±22	0·0014044	±21

Thus, silicon tetrachloride has a density of 1·481475 with a calculated probable error of $\pm 0{\cdot}0_5 68$, and a coefficient of thermal expansion of 0·0014044 with a calculated probable error of $\pm 0{\cdot}0_6 87$.

Evidently the application of these corrections leaves unaltered

the relative atomic weights derived from the densities, and does not affect our previous conclusion that silicon shows no greater variation than 0·005 unit in the samples examined.

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[*Received, October* 13*th*, 1926.]

CCCCXXVII.—*The Thermal Reactivity of Ozone in Presence of Hydrogen.*

By JOSEPH WATKIN BELTON, ROBERT OWEN GRIFFITH, and ANDREW MCKEOWN.

IN a previous communication (Griffith and McKeown, J., 1925, **127**, 2087) it was noted that helium, argon, nitrogen, and carbon dioxide exert a definite positive catalytic effect on the rate of thermal decomposition of ozone at 100°, whilst oxygen retards the deozonisation. We have now extended the measurements to include the effect of hydrogen on the same reaction. The interpretation of the results is in this case complicated by the simultaneous formation of water by reaction between hydrogen and ozone; the only publication relating to this thermal reaction, so far as we are aware, is that of Pickel (*Z. anorg. Chem.*, 1904, **38**, 307), who established qualitatively its occurrence at temperatures between 80° and 226°. Data of a more quantitative character have been obtained for the corresponding photochemical reaction—in ultra-violet light by Weigert and Böhm (*Z. physikal. Chem.*, 1915, **90**, 194) and in the visible region by Griffith and Shutt (J., 1923, **123**, 2752). In both cases, hydrogen, in addition to reacting with part of the ozone to give water, produces a marked accelerating effect on the deozonisation process itself. For example, in the experiments of Griffith and Shutt a mixture of hydrogen, oxygen, and ozone at ordinary pressure and containing 20% of hydrogen had an intrinsic rate of deozonisation about four times that obtained in the absence of hydrogen. This increase is considerably greater than that found with corresponding amounts of any of the gases helium, argon, nitrogen, and carbon dioxide for both the thermal and the photochemical mode of decomposition, but is of the same order of magnitude as the positive catalytic effect of hydrogen now obtained for the thermal decomposition.

EXPERIMENTAL.

The apparatus and the experimental method were essentially those employed by Griffith and McKeown (*loc. cit.*). Ozonised

oxygen was generated by the method of Fischer and Massenez, which with suitable anode cooling gave a yield of ozone up to 10—11% by volume. Hydrogen was prepared by the electrolysis of a sodium hydroxide or baryta solution. The gases, collected in approximately the required proportions, were mixed and dried over-night above concentrated sulphuric acid. The exact composition of the system before reaction was obtained as follows: The ozone content of a known volume was determined iodometrically, and the hydrogen content by collecting a sample of the mixture over potassium iodide solution and sparking over water.

The glass reaction tube (Tube D of the previous communication; *loc. cit.*, p. 2088) always contained 3—5 c.c. of concentrated sulphuric acid spread along its whole length and covering about one-eighth of its inner surface. Since no part of the gaseous phase was more than 2 cm. distant from the acid surface, this disposition was considered efficient for the immediate removal of water vapour from the gaseous phase. Observations were made at two temperatures, approximately 78° and 100°, by using alcohol vapour or steam for jacketing the reaction- and compensator-tubes. The total pressure of the system (measured at 100°) ranged between 400 and 1000 mm. Hg; the content of hydrogen was varied between 2 and 50%, and the ratio of oxygen to ozone in the gas was usually about 11.

The course of the reaction was followed by time readings of the pressure increase or decrease of the system as registered by a sulphuric acid manometer. The pressure change is the sum of two opposite effects, the process of deozonisation being attended by an increase of pressure, whilst the reaction between hydrogen and ozone, with absorption of the resultant water, is accompanied by a decrease. Of special significance for purposes of calculation are (1) the maximum pressure usually attained at some time during the course of a run, and (2) the final pressure reached when all the ozone has reacted. Actually a maximum pressure was obtained only when the initial hydrogen concentration was within certain limits relative to the ozone concentration. With very low hydrogen concentrations, the pressure increased progressively and the theoretical maximum was not reached in the time of observation—usually 3—5 hours. With high hydrogen concentrations, the pressure decreased from the beginning, and either a maximum was not theoretically possible, or it occurred so near the start that it escaped detection. (On raising the temperature of the system, before significant readings could be taken, a few minutes were always necessary to allow the reaction- and compensator-tubes to attain a uniform temperature.) At 78°, where the rate of reaction is

much slower, the upper limit of hydrogen concentration, for which a pressure maximum could be recorded, was higher than at 100°.

Interpretation of Experimental Data.—In certain cases, a check on the manometric readings was attempted by direct analysis of the system for ozone and hydrogen after the reaction had proceeded to a considerable extent. The results of the six experiments for which this was done are in Table I, in which p is the observed pressure change (in mm. of sulphuric acid), a and a' the initial and the final concentration of ozone (g.-mol. per litre), and b and b' the initial and the final concentration of hydrogen. All except the last of these experiments were carried out at 100°.

TABLE I.

p.	a.	a'.	b.	b'.	b' (calc.).
+20·0	0·001757	0·000042	0·004948	0·004419	0·004454
+49·5	0·003102	0·000016	0·006726	0·005879	0·005889
−16·8	0·001753	0·000055	0·007232	0·006560	0·006601
− 7·1	0·001551	0·000115	0·006472	0·005890	0·005964
+ 4·1	0·002140	0·000021	0·006570	0·005812	0·005879
−35·5	0·001670	0·000155	0·01048	0·009738	0·009837

The table shows that, whilst an appreciable amount of hydrogen reacts, the change in the concentration of hydrogen is always less than that of ozone. The figures in the last column were calculated in the following manner. In addition to the reaction (2) $2O_3 \longrightarrow 3O_2$, there takes place a water-forming reaction which may be either (1) $H_2 + O_3 \longrightarrow H_2O + O_2$, or (1′) $3H_2 + O_3 \longrightarrow 3H_2O$. Assuming that (1) is the reaction which occurs, then the disappearance of $(b—b')$ mols. of hydrogen involves a pressure decrease (the water formed being absorbed by sulphuric acid) of $A(b—b')$, where A is a calculable constant. The total ozone reacting is $(a—a')$ mols., of which $\{a—a'—(b—b')\}$ mols. react according to (2), involving a pressure increase of $A\{a—a' — (b—b')\}/2$. The net pressure change is thus $A\{a—a' — (b—b')\}/2 — A(b—b')$, *i.e.*, $A\{a—a' — 3(b—b')\}/2$. Equating this to the observed pressure change p, and substituting the values of a, a', and b, the value of b', that is the final concentration of hydrogen, can be calculated.

There is a systematic discrepancy of about 1% between the calculated and the observed values of b'. In all probability this error is inherent in the experimental measurement of the final concentration of hydrogen, since the sample for analysis could be taken conveniently only from the reaction-tube maintained at 100° (or 78°), and containing the reacting system at a pressure greater than atmospheric. The hydrogen content obtained would tend to be too low owing to failure to obtain a representative sample of the gas mixture. An alternative cause of the discrepancy would

be the partial formation of hydrogen peroxide, but the necessary assumption that the peroxide should remain undecomposed in the gaseous phase in the presence of ozone is untenable. Unfortunately, the other stoicheiometric possibility (1′), taken in conjunction with (2), leads to exactly the same calculated values of b' as in the table above, so that analytically it is impossible to differentiate between the mechanisms (1) and (1′) for the disappearance of hydrogen. Thus, assuming reactions (2) and (1′) to occur, the pressure decrease associated with the disappearance of $(b—b')$ mols. of hydrogen is now $4A(b—b')/3$, and the pressure increase due to the deozonisation of the remaining $\{a—a' - \frac{1}{3}(b—b')\}$ mols. of ozone is $A\{a—a' - \frac{1}{3}(b—b')\}/2$. The net pressure change is thus $A\{a—a' - 3(b—b')\}/2$ as before. From the kinetic point of view, however, reaction (1) is much more probable than (1′). If reaction (1′) does occur, it will be a two-stage reaction of the type:

$$\begin{cases} (a)\ O_3 + H_2 \longrightarrow H_2O + O_2(\text{activated}) \\ (b)\ O_2(\text{activated}) + 2H_2 \longrightarrow 2H_2O \\ \qquad\qquad \text{or possibly} \\ (c)\ O_2(\text{activated}) + H_2 \longrightarrow H_2O_2 \\ (d)\ H_2O_2 + H_2 \longrightarrow 2H_2O \text{ or } 2H_2O_2 \longrightarrow 2H_2O + O_2. \end{cases}$$

Another conceivable alternative for (d) would be (e) $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$, which, in conjunction with (a) and (c), is equivalent to (1). In view of these complications, all of which it would be impossible to take into account in the kinetic treatment, we have deemed it best to base our calculations on the assumption that only reactions (1) and (2) occur. If any of the reactions (b), (c), and (d) do take place, a certain error will be introduced into the values calculated below for the intrinsic rates of reaction (2) and the reaction forming water. The error for the former cannot be very serious in the experiments with not too high partial pressures of hydrogen, and it will be in such a direction as to give too small values for the velocity coefficient k_2 of the deozonisation reaction (2). On the other hand, our calculated values of k_1, the velocity coefficient for reaction (1), will be too high if reactions (b), (c), and (d) occur; here the error will be greater, up to a maximum of three times the calculated velocity coefficient.

We assume that the two simultaneous reactions (1) and (2) conform to the bimolecular law. This is at least approximately true for the latter process in the absence of hydrogen and in tubes free from catalysing action, although the absolute value for the velocity coefficient depends upon the concentrations of oxygen and other non-reactive gases present. If the presence of hydrogen also affects the velocity of (2), this effect will probably be manifested in

the variation of the velocity coefficient with varying initial concentration of hydrogen, but the small change in the concentration of hydrogen throughout any particular run can produce very little trend in the coefficients obtaining for that run.

Accordingly, if x and y represent the amounts of ozone which have reacted after a time t according to (1) and (2), respectively, then

$$dx/dt = k_1(a - x - y)(b - x) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$dy/dt = k_2(a - x - y)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$p_t = A(\tfrac{1}{2}y - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where p_t is the change in pressure of the system (at constant volume) and A, a, b, k_1, and k_2 are as already specified. Since we do not know x and y separately at various times during a run, the evaluation of k_1 and k_2 can be effected only by an indirect process which is both involved and laborious. From (3) and (4) we obtain

$$dy/dx = k_2(a - x - y)/k_1(b - x) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

the solution of which (with initial conditions $x = 0$, $y = 0$) is

$$y = a - x + \frac{b - x}{K - 1} - \left\{\frac{(K - 1)a + b}{K - 1}\right\}\left(\frac{b - x}{b}\right)^K \quad . \quad (7)$$

where K is written for the ratio k_2/k_1. It is now possible to evaluate K, either from the conditions obtaining at the maximum of pressure (p_m) or from the final conditions when all the ozone has disappeared.

In the first case, at the moment when the pressure has attained a maximum value, the rate of disappearance of ozone according to reaction (2) must be just double its rate of disappearance according to (1), so that

$$2 = K_m(a - x_m - y_m)/(b - x_m) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where the suffix m refers to conditions at the maximum. This equation, combined with

$$p_m = A(\tfrac{1}{2}y_m - x_m) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5')$$

and

$$y_m = a - x_m + \frac{b - x_m}{K_m - 1} - \left\{\frac{(K_m - 1)a + b}{K_m - 1}\right\}\left(\frac{b - x_m}{b}\right)^{K_m} . \quad (7')$$

leads to

$$\{(3b - a_1)K_m/b(3K_m - 2)\}^{K_m} = (3b - a_1)/\{(K_m - 1)a + b\} . \quad (9)$$

in which $a_1 = a - 2p_m/A$, from which the value of K_m can be obtained by trial.

At the end, when the pressure has become constant and all the ozone has reacted (suffix ∞), we have

$$x_\infty + y_\infty = a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$p_\infty = A\{\tfrac{1}{2}y_\infty - x_\infty\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5'')$$

from which x_∞ and y_∞ separately can be calculated. By substitution of the value of x_∞ in the equation

$$b = \{(K_\infty - 1)a + b\}\left(\frac{b - x_\infty}{b}\right)^{K_\infty - 1} \quad . \quad . \quad . \quad (11)$$

which results from (10) and (7''), *i.e.*, the form assumed by (7') for $t = \infty$, the value of K_∞ also can be obtained by the method of trial and error.

The possibility of a preliminary test of the kinetic equations (1) and (2) is now available, since the values of K_m and K_∞ calculated as above for any particular experiment should be equal. The last two columns of Table II show that a fair agreement exists in every case between these ratios of velocity coefficients, referring as they do to two very different epochs in the history of the reacting system. The value of K_∞ is in nearly every case slightly less than the corresponding value of K_m. The latter is likely to be the more accurate, since K depends ultimately upon the relevant pressure reading (an error of about 1 mm. in this affects the value of K by nearly half a unit in most cases), and usually the final pressure difference had to be extrapolated from a knowledge of the last pressure difference read and the slight residual concentration of ozone in the reaction tube when reaction was stopped.

However, the agreement between K_m and K_∞ does not necessarily imply that (3) and (4) constitute a correct mathematical statement of the kinetic laws, since neither equation separately, but only their combination in (5), is used for the derivation of equations (9) and (11). Any alternatives to (3) and (4) which would also lead to (5) would be equally well supported by this agreement. It is necessary to calculate the separate velocity coefficients, k_1 and k_2, and to find whether these, as well as their ratio, remain constant throughout the course of the two simultaneous reactions. An analytical solution of the differential equations to give, say, k_1, as a function of the variables p and t is not possible. We have therefore resorted to the following indirect method. Knowing K from the final, or preferably the maximum, conditions, the values of y and p corresponding to a series of values of x are calculated from (7) and (5), respectively. These are plotted against x and from the graphs the values of x and y corresponding to any observed pressures p at a known time t are read off. From the series of (x, y, t) data thus obtained, equations (3) and (4) can now be solved

approximately for k_1 and k_2 by the method of finite differences. The values thus obtained are given below.

In the tables, P represents the total pressure of the system, p_{O_2} and p_{H_2} the partial pressures of oxygen plus ozone and of hydrogen respectively (all calculated for 100° in mm. Hg) at the start of an experiment, and c the initial concentration of oxygen in g.-mols. per litre. The coefficients k_1 and k_2 are in absolute units (litres/mols.-minutes) and have been corrected from the temperature of experiment (lying for the two series of data within the limits 99·3—100·3° and 77·7—78·2°) to the common temperature of 100° or 78°—this correction amounts in no case to more than a few units per cent. In general, the velocity coefficients calculated throughout a run vary irregularly by not more than 15% from the mean value tabulated. However, with concentrations of hydrogen higher than that corresponding to a partial pressure of about 200 mm., there is always a definite decrease of both k_1 and k_2 as the reaction proceeds; this tendency is indicated by tabulating the limits of such falling coefficients.

TABLE II.

Hydrogen–Oxygen–Ozone Mixtures at 100°.

Expt. No.	P.	p_{O_2}.	p_{H_2}.	$a.10^6$.	$b.10^6$.	$c.10^5$.	k_1.	k_2.	K_∞.	K_∞.
46	759·6	743·6	16·0	2007	689	2995	0·83	18·4	(22)	—
47	758·0	725·4	32·6	2479	1402	2870	1·14	23·0	20·22	—
43	767·8	722·3	45·5	3052	1955	2754	1·15	26·0	22·5	22·5
25	766	720·4	45·6	2597	1962	2811	1·60	28·6	17·83	15·7(?)
44	764·3	714·5	49·8	2952	2142	2776	1·17	26·5	22·5	—
48	757·4	706·7	50·7	2224	2181	2815	1·35	27·9	21·3	—
49	759·3	687·2	72·1	2069	3100	2746	1·93	36·8	19·2	—
36	768·6	691·7	76·9	2627	3332	2705	1·81	36·3	20·5	20·9
26	757·5	680·1	77·4	2701	3327	2655	2·02	37·0	18·46	17·75
27	996·6	918·6	78·0	3778	3354	3572	1·72	32·6	18·85	18·0
28	498·5	420·4	78·1	1556	3360	1652	2·60	51·9	20·0	—
29	494·3	415·7	78·6	1503	3376	1637	2·57	49·6	19·3	—
30	493·3	414·1	79·0	1625	3424	1615	2·67	53·1	20·23	18·6
31	988·3	895·4	92·9	3457	3999	3505	2·15	37·2	17·4	17·2
37	501·9	404·8	97·1	1473	4170	1591	2·78	60·4	21·5	21·0
50	841·8	728·2	113·6	2211	4884	2908	2·45	46·0	18·7	—
32	760	636·8	123·2	2032	5295	2532	2·61	47·8	18·2	17·25
38	1014	878	136·0	2917	5858	3480	2·60	53·3	20·55	19·6
52	977·0	824·1	152·9	2140	6570	3329	3·27	55·2	17·25	16·9
33	985·8	829·4	156·4	3102	6727	3256	3·19	54·8	17·15	16·5
39	786·0	629·5	156·5	2261	6515	2498	3·29	60·5	18·3	18·5
40	1029	868·2	160·8	3212	6908	3406	2·93	54·4	18·6	—
53	975·0	806·8	168·2	1753	7232	3292	3·37	56·9	17·2	16·9
41	1018	883	185·0	3075	7965	3270	3·47	62·9	18·1	—
34	753·5	459·5	294	1595	12650	1818	5·7–4·0	104–73	(18·25)	18·25
45	757·9	392·7	365·2	1374	15690	1551	11·5–4·6	200–80	(17·36)	17·36
*35	998·6	421·0	69·6	1645	2997	1645	3·17	60·7	19·06	18·2

* In this experiment argon also was present, its concentration being 2183×10^{-5} g.-mol./litre.

TABLE III.

Hydrogen–Oxygen–Ozone Mixtures at 78°.

Expt. No.	P.	p_{O_2}.	p_{H_2}.	$a \cdot 10^6$.	$b \cdot 10^6$.	$c \cdot 10^5$.	k_1.	k_2.	K_m.*
10	761·2	743·7	17·5	2645	752·5	2932	0·074	1·69	(22·5)
11	329·5	311·8	17·7	1049	761·9	1236	0·135	3·06	(22·5)
12	759·6	727·8	31·77	2549	1366	2873	0·109	2·39	(22·0)
13	754·2	707·7	46·53	2390	2000	2803	0·150	3·31	(22·0)
14	758·6	706·2	52·4	2307	2253	2804	0·158	3·47	22·0
15	760·6	686·0	74·6	2228	3208	2725	0·227	4·65	20·4
16	500·2	421·8	78·44	1152	3372	1698	0·287	6·36	22·1
18	799·9	718·5	78·6	2279	3381	2872	0·256	5·41	21·1
17	501·1	420·8	80·26	1368	3450	1672	0·300	6·66	22·3
19	998	916·5	81·45	3190	3501	3620	0·216	4·56	21·22
20	830·4	720·7	109·7	2291	4716	2869	0·323	6·64	20·42
21	870·4	722·5	147·9	1883	6353	2917	0·461	8·86	19·3
22	918·8	718·5	200·3	1944	8610	2895	{0·68– 0·4}	{12– 7}	17·9
23	971·4	726·4	245	1963	10530	2927	{0·86– 0·4}	{15– 7}	17·9
24	1001	726·4	274·6	1897	11810	2931	{1·1– 0·4}	{20– 6}	17·6
54	978	734·3	243·7	1670	10480	2989	{0·62– 0·38}	{10·6– 6·4}	16·9

* Values of K_m in parentheses have been assumed for the purpose of calculating k_1 and k_2.

Discussion of Results.

The Ratio k_2/k_1.—Whilst the two values of this ratio, *viz.*, K_m and K_∞, which can be directly calculated for each experiment are equal within the limits of our accuracy, the same agreement does not hold between the values of K referring to widely different reacting systems. Since, for any one reacting system the hydrogen and oxygen concentrations remain approximately constant, whilst the ozone concentration varies, we may conclude that K is independent of ozone but not of hydrogen or oxygen concentrations. With increasing concentration of hydrogen there is a decrease in the value of K from about 22 to 17. It is impossible to say whether or not it depends also upon the concentration of oxygen present. Again, for the same system there is no definite difference between the values of K at the two temperatures 100° and 78°, so that the temperature coefficients of the two reactions (1) and (2) are approximately identical.

The Velocity Coefficients.—The fact that K is not a constant independent of the composition of the reacting mixture implies that the two kinetic equations (3) and (4) are not sufficiently comprehensive in respect of the dependence of the speeds of reaction on the concentration of hydrogen and possibly also on that of oxygen; this is also evident from the marked dependence of k_1 and k_2 on the composition of the reaction mixture. With a constant partial pressure of oxygen of about 700 mm., the coefficient

k_2 of the deozonisation process increases from its normal value of 10·4 in the absence of hydrogen to about 60 for a partial pressure of hydrogen of 150 mm., and k_1 increases simultaneously, although not quite so rapidly. On the other hand, with constant partial pressure of hydrogen, the velocity coefficients definitely decrease with increasing concentration of oxygen. In Tables IV and V are summarised a few data which serve to illustrate these effects.

TABLE IV.

Variation of k_1 and k_2 with p_{H_2}.

Expt. No.	p_{O_2}.	p_{H_2}.	k_1.	k_2.
$t = 100°$. $p_{O_2} = 680$—730 mm.				
—	705	—	—	10·4
47	725	32·6	1·14	23·0
43	722	45·5	1·15	26·0
44, 48	711	50·3	1·26	27·2
26, 36, 49	686	75·5	1·92	36·7
50	728	113·6	2·45	46·0
$t = 100°$. $p_{O_2} = 860$—920 mm.				
—	890	—	—	8·6
27	919	78·0	1·72	32·6
31	895	92·9	2·15	37·2
38	878	136·0	2·60	53·3
40	868	160·8	2·93	54·4
41	883	185·0	3·47	62·9
$t = 78°$. $p_{O_2} = 700$—740 mm.				
—	720	—	—	1·02
10	744	17·5	0·074	1·69
12	728	31·8	0·109	2·39
13	708	46·5	0·150	3·31
14	706	52·4	0·158	3·47
18	719	78·6	0·256	5·41
20	721	109·7	0·323	6·64
21	723	147·9	0·461	8·86

TABLE V.

Variation of k_1 and k_2 with p_{O_2}.

Expt. No.	p_{H_2}.	p_{O_2}.	k_1.	k_2.
$t = 100°$. $p_{H_2} \leftrightarrows 78$ mm.				
28, 29, 30	78·6	417	2·65	51·5
26, 36	77·2	686	1·92	36·7
27	78·0	919	1·72	32·6
$t = 100°$. $p_{H_2} \leftrightarrows 156·5$ mm.				
39	156·5	630	3·29	60·5
33	156·4	829	3·19	54·8
$t = 78°$. $p_{H_2} \leftrightarrows 17·6$ mm.				
11	17·7	312	0·135	3·06
10	17·5	744	0·074	1·69
$t = 78°$. $p_{H_2} \leftrightarrows 80$ mm.				
16, 17	79·4	421	0·294	6·51
18	78·6	719	0·256	5·41
19	81·5	917	0·216	4·56

One of the most striking results of this work is the very strong catalytic effect of hydrogen on the reaction $2O_3 \longrightarrow 3O_2$, compared with that of the inert gases helium and argon. Thus at 100°, the value of k_2 in a mixture of ozonised oxygen with helium ($p_{O_2} = 400$ mm., $p_{He} = 600$ mm.) is about 17, in a mixture with argon ($p_{O_2} = 400$ mm., $p_A = 600$ mm.) about 22, whilst in a mixture with the same partial pressure of oxygen but with a partial pressure of hydrogen of only 78 mm., the value of k_2 is 51. This very much greater catalytic effect of hydrogen has also been observed for the photochemical reaction in visible light. The values given in the tables for k_2 are minimum values, for, if the stoicheiometric process (1′) occurs to any extent our calculated values become too small. Moreover, the establishing of the large increase in k_2 caused by the

presence of hydrogen is not dependent on the special assumptions made in the interpretation of our experimental data: confirmation may be obtained from the initial pressure readings in experiments with small partial pressures of hydrogen. Under such conditions, the reaction $2O_3 \longrightarrow 3O_2$ takes place with an initial velocity considerably greater than that of the formation of water; we may thus, with small error, neglect any pressure decrease due to the latter and equate the observed increase of pressure to that caused by the deozonisation reaction. Values of k_2 have been obtained in this way for Expts. 10—14: they agree very well with those given in Table III; naturally, owing to neglect of the water-forming reaction, they are in all cases slightly lower—usually about 10%. Confirmation of the catalytic effect of hydrogen was also obtained from the results of an experiment in which sulphuric acid was omitted from the reaction tube and the water remained as vapour. The partial pressure of hydrogen was 150 mm., that of oxygen 610 mm., and the temperature 100°. The increase in pressure at the start is a measure of the extent of the reaction $2O_3 \longrightarrow 3O_2$, since the reaction $O_3 + H_2 \longrightarrow H_2O + O_2$ is now unattended by any pressure change.* The initial value thus obtained for k_2 was 86, which is somewhat greater than the value 60·5 given in Table II for Expt. 39 in which the initial partial pressures of hydrogen and oxygen were comparable with those in the present instance. This greater value is probably due to the known fact that water vapour catalyses the decomposition of ozone.

The data of any one section of Table IV give a straight line when k_2 is plotted against p_{H_2}, within the limits of the rather large experimental error; thus $k_2 = k_2^\circ + B \cdot p_{H_2}$, where k_2° is the velocity coefficient in absence of hydrogen and B is a constant. Both k_2° and B, however, are functions of the partial pressure of oxygen. An empirical expression for the dependence of k_2° on p_{O_2} has already been given (Griffith and McKeown, *loc. cit.*, p. 2092). The coefficient B certainly decreases with increasing partial pressure of oxygen, possibly in a manner similar to k_2°, but our results are not sufficiently accurate to enable us to deal quantitatively with this point.

Table II includes the results of Expt. 35 in which argon was also present; the velocity coefficient k_2 in this case is certainly greater than the value which would have been obtained in the same system in the absence of argon, but the relative smallness of the effect would suggest either that argon affects the term k_2° only, or that its effect on the coefficient B is slight.

In view of the doubt as to whether the stoicheiometric process

* If the reaction $O_3 + 3H_2 \longrightarrow 3H_2O$ takes place, it would cause the calculated value of k_2 to be too low.

(1′) actually occurs or not, the values tabulated for k_1 are subject to a much greater possible error than those of k_2. There is no doubt, however, that the value of k_1 is considerably smaller than that of k_2, and also that the conditions which favour an increase in k_2 have a similar effect on k_1, so that the two reactions, the deozonisation process and the formation of water, are coupled in some way.

Temperature Coefficients and Reaction Mechanism.

The temperature coefficient of k_2 in the absence of hydrogen was determined (for three different partial pressures of oxygen) by following the pressure change of the same system for some time at 78° and then at 100°. The results are given in Table VI.

TABLE VI.

p_{O_2}.	k_2 ($t = 100°$).	k_2 ($t = 78{\cdot}1°$).	E.
332	17·8	1·70	27,960
743	9·5	0·925	27,750
1010	7·72	0·76	27,600

The values calculated for E are derived from the Arrhenius equation $d \log k_2/dT = E/RT^2$; they correspond to a temperature coefficient k_{t+10}/k_t of 2·9. The mean value of E is 27,770 cals., as compared with 26,740 (Warburg, *Ann. Physik*, 1902, **9**, 1286) and 26,130 (Clement, *ibid.*, 1904, **14**, 342). The temperature coefficient of k_2 (and also that of k_1) decreases with increasing partial pressure of hydrogen. Thus, with $p_{H_2} = 78$ mm. and $p_{O_2} = 710$ mm. the value of E is 23,700 cals., corresponding to a temperature coefficient of 2·48. Values of the latter intermediate between 2·9 and 2·48 are obtained with lower partial pressures of hydrogen. The temperature coefficients of $k_2°$ and B (see p. 3162), as deduced from the data at 78° and 100°, are 2·9 and 2·4 respectively, and thus the temperature coefficient of k_2 for any reaction mixture containing hydrogen will lie between these limits, becoming 2·4 in presence of a large excess of hydrogen. The temperature coefficient of k_1 varies similarly.

The temperature coefficient 2·9 for the deozonisation reaction in absence of hydrogen is much higher than what would be expected for a homogeneous bimolecular reaction taking place with measurable speed at 100°. Using the well-known kinetic expression for the velocity coefficient of such a reaction,

$$k_2 = 2\sigma^2\sqrt{\frac{4\pi RT}{M}} \cdot \frac{N_0}{1000} \cdot e^{-E/RT} \quad . \quad . \quad . \quad (12)$$

[in which σ = the diameter of the ozone molecule (taken as $2{\cdot}10 \times 10^{-8}$ cm.), $N_0 = 6{\cdot}06 \times 10^{23}$, and $E = 27{,}770$], k_2 is found

to be of the order 10^{-4} (in the units used) at 100°, whereas the experimental values of k_2 are about 100,000 times greater. To account for our observed velocity coefficients on the basis of the above equation, we should have to employ a value $E = 19{,}000$ cals. (approx.). This discrepancy appears to be much greater than any possible experimental error. It may be suggested that in these experiments it is not a homogeneous change but mainly a "wall" reaction which is being measured; but, if this were so, the true value of E (for the homogeneous change) would be still greater than 27,700 cals. and no detectable decomposition of ozone at 100° by a homogeneous change should be possible. Chapman and Clarke (J., 1908, **93**, 1638), however, found an easily measurable rate of decomposition at this temperature, the rate being independent of the ratio area/volume of the reaction vessel, so that the measured reaction was predominantly homogeneous. Moreover, our velocity coefficients at 100° are nearly equal to those calculated from the data of Chapman and Clarke (*loc. cit.*) and of Chapman and Jones (J., 1910, **97**, 2463). The above suggestion is therefore not valid.

Granted that the change is homogeneous, a solution of the difficulty might perhaps be obtained by the following considerations. The equation (12) for the velocity coefficient is based on the assumption that all the energy increment of 27,700 cals. necessary for reaction is associated, before collision, with a single degree of freedom of one of the reacting molecules; a velocity coefficient of essentially the same magnitude also follows from the assumption that the total energy of activation is derived from the translatory energy of the colliding molecules. A very much greater value of k_2 can, however, be obtained if it be assumed that the total energy of activation is shared, before collision, between a number of degrees of freedom (external and internal) of the reacting molecules. For example, limiting ourselves to the internal degrees of freedom, if these be n in number for each of the colliding ozone molecules, the expression (12) would be multiplied by $(E/RT)^{n+1}/\underline{|n+1}$ (compare Rideal and Lewis, *J. Amer. Chem. Soc.*, 1926, **48**, 2559). Since E/RT in the present case lies between 37 and 40, it would only be necessary to assume $n = 3$, thus making this multiplying factor of the order of 10^5, to account for the discrepancy; this could be interpreted in the sense that the energy of activation is resident in the six degrees of freedom either of rotation or of vibration of the two colliding ozone molecules.

An alternative possibility is that the deozonisation process involves a "chain" mechanism in somewhat the same sense as postulated by Christiansen and Kramers (*Z. physikal. Chem.*, 1923, **104**, 451) for the case of unimolecular reactions. The decomposition

of ozone is certainly sufficiently exothermic to permit of the resultants having an excess energy greater than that necessary for the activation of fresh reactants. But whilst the possibility of short reaction-chains cannot be ignored, the moderate quantum yields obtained in the corresponding photochemical process (where the resultant oxygen molecule would possess excess energy in even greater amounts) make it highly improbable that in the thermal process the reaction-chains could be of the enormous length required to account for the discrepancy.

In a previous paper (Griffith and McKeown, *loc. cit.*), a formal mechanism for the thermal decomposition of ozone was suggested involving the reaction stages (α) $O_3 \longrightarrow O_3^*$; ($\beta$) $O_3^* + O_3 \longrightarrow$ complex; (γ) complex $\longrightarrow 3O_2$, together with the assumption that (γ) and the reversal of (β) could take place either spontaneously or by collision of the complex with other molecules, the nature of which decided the relative probabilities of these changes. The addition to the system of hydrogen, which has an accelerating effect much greater than that of helium, argon, or nitrogen, introduces a complication, *viz.*, the simultaneous occurrence of the reaction $H_2 + O_3 \longrightarrow H_2O + O_2$. The fact that this process is coupled in some way with the deozonisation reaction would suggest, as a possible explanation of the catalytic effect of hydrogen, the formation of an intermediate compound (H_2O_3) which could decompose in two ways (ε and ζ), either to form water or to yield oxygen. Thus, in the presence of hydrogen, in addition to reactions (α), (β), and (γ), the following would also occur :

(δ) $H_2 + O_3^* \longrightarrow$ complex;
(ε) Complex $+ O_3 \longrightarrow 3O_2 + H_2$;
(ζ) Complex $+ H_2 \longrightarrow H_2O + O_2 + H_2$.

In order to obtain a qualitative agreement with our experimental data, it is further necessary that the complex (H_2O_3) should decompose to yield water only on collision with a hydrogen molecule. The complete scheme entails deozonisation by reactions (γ) and (ε).

However, the effect of hydrogen upon the complex (O_6) molecule resulting from stage (β) must also be considered. By analogy with the cases of argon, helium, and nitrogen it is probable that the stage (γ) will be catalysed to some degree by collision of the complex with hydrogen molecules; but there is also the possibility that such collisions will occasionally lead to water formation: $H_2 + (O_6) \longrightarrow H_2O + O_2 + O_3$. The occurrence of this last process to any extent would enhance the coupling between the net deozonisation and the net water-formation, and make the ratio of the coefficients

k_2/k_1 much less dependent on the partial pressure of hydrogen than would otherwise be the case.

On the basis of these considerations, the observed variation of the temperature coefficient of k_2 (and also of k_1) with the hydrogen content implies a difference in the temperature coefficients of the primary reactions which yield the two complexes (O_6) and (H_2O_3). The temperature coefficient for the first is 2·9, that for the second is 2·4 (the value obtained with a large excess of hydrogen), and if deozonisation takes place through the medium of both the complexes, the observed temperature coefficient in any mixture will lie between these limits. The same conclusion applies to the observed temperature coefficient of the water-forming reaction, provided that this also involves collision of the (O_6) complex with hydrogen.

Summary.

Reaction-velocity measurements have been made in mixtures of ozone, oxygen, and hydrogen at 78° and 100°. Two reactions occur —the deozonisation process $2O_3 \longrightarrow 3O_2$, and a water-forming reaction which is most probably $H_2 + O_3 \longrightarrow H_2O + O_2$.

The values of k_2 and k_1, the respective bimolecular velocity coefficients, both increase markedly with increasing partial pressure of hydrogen, but decrease with increasing partial pressure of oxygen. The ratio k_2/k_1 varies relatively slightly with the composition of the gas mixture, lying between 22 and 17 at both temperatures.

The temperature coefficient of k_2 in the absence of hydrogen is 2·9; in the presence of excess of hydrogen it is reduced to 2·4.

A discussion of these results and a possible explanation of the coupling of the two reactions are given.

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CCCCXXVIII.—*Acid and Salt Effects in Catalysed Reactions. Part III. Dependence of the Characteristics of the Minimum-Velocity Mixture on the Concentration of the Acid and the Application of Minimum Velocity to the Determination of Catalytic and Ionisation Constants.*

By HARRY MEDFORTH DAWSON and CHARLES RANDALL HOSKINS.

IN Part II of this series (Dawson and Dean, this vol., p. 2872) it was shown that the curve obtained by plotting reaction velocity against the p_H value of catalysing mixtures of the type cHA +

xMA is symmetrical with respect to the point at which the reaction velocity has a minimum value. Denoting the catalytic coefficients for the hydrogen ion, the acid ion, and the undissociated acid molecule by k_h, k_a, and k_m, respectively, and the ionisation constant by K, it was shown that the hydrogen-ion concentration of the minimum-velocity (*M.V.*) mixture is given by

$$[\mathrm{H}]_i^+ = \sqrt{k_a Kc/(k_h - k_m)} \quad . \quad . \quad . \quad . \quad (1)$$

and the corresponding reaction velocity by

$$v_i = 2\sqrt{(k_h - k_m)k_a Kc} + k_m c \quad . \quad . \quad . \quad . \quad (2)$$

For each series of acid–salt mixtures for which the concentration of the acid is constant, the observed changes in velocity are due entirely to the hydrogen and acid ions, and if the minimum value of this ionic reaction velocity is denoted by $u_i = v_i - k_m c$, it follows from (1) and (2) that

$$u_i/[\mathrm{H}]_i^+ = (v_i - k_m c)/[\mathrm{H}]_i^+ = 2(k_h - k_m) \quad . \quad . \quad (3)$$

The object of this paper is to show that the experimental data for the acetone–iodine reaction under the catalysing influence of mixtures of acetic acid and sodium acetate are in general agreement with the above equations.

Dependence of $[\mathrm{H}]_i^+$ *on the Concentration of the Acid.*

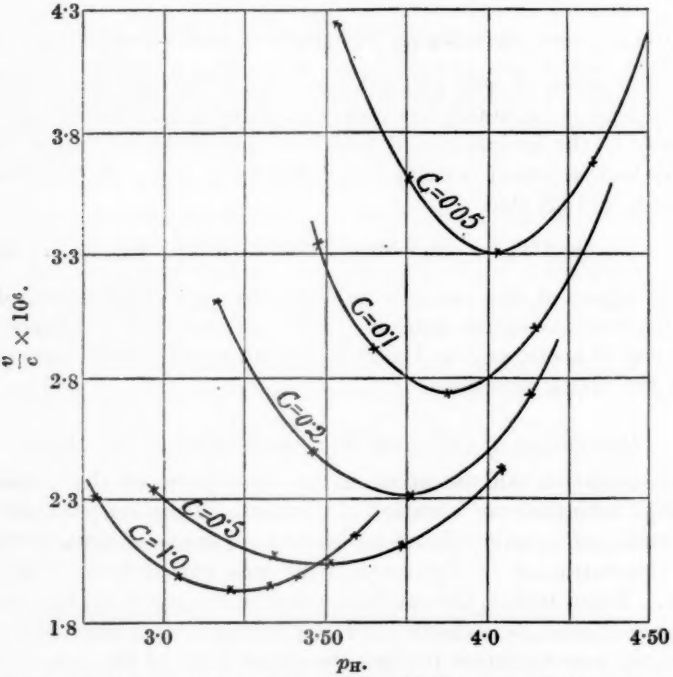
Consideration will be given in the first place to the variation of $[\mathrm{H}]_i^+$ with the concentration of the acid. The data available for the testing of equation (1) are those obtained in experiments in which the concentration of the acetic acid was varied from 0·01N to 1·0N. Below 0·01N, the catalytic effect of the hydroxyl ion cannot be ignored, and, as is shown later, disturbing factors come into play when the concentration reaches the upper limit of the series. For the acid–salt mixtures with 0·2 and 0·05N-acid, the measurements recorded by Dawson and Carter (this vol., p. 2282) and by Dawson and Dean (*loc. cit.*) have been utilised for the purpose of testing the equation.

In the actual determination of $[\mathrm{H}]_i^+$, advantage has been taken of the fact that the v–p_{H} curves are symmetrical with respect to the *M.V.* point. It may be noted, however, that $[\mathrm{H}]_i^+$ may also be derived from the curves which are obtained by plotting the reaction velocity against the logarithm of the concentration of the salt. Such v–log x curves give that value of x, namely x_i, for which the reaction velocity is a minimum, and since the value of $[\mathrm{H}]_i^+$ may be neglected in comparison with x_i, it follows that the hydrogen-ion

concentration of the *M.V.* mixture may be derived from $[H]_i^+ = Kc/x_i$.

The variation of $(p_H)_i$ with the concentration of the acid is shown in the accompanying diagram. In order to reduce the distortion which shows itself when the velocity–p_H curves are directly compared, the curves which are actually shown in the diagram are those obtained by plotting the specific reaction velocity v/c against p_H

FIG. 1.



Specific velocity curves for mixtures $cCH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$ *showing the dependence of the velocity and the hydrogen-ion concentration of the* M.V. *mixtures on the concentration (c) of the acid.*

for concentrations of acid from 0·05 to 1*N*. The p_H values are those given by the mass-law expression $p_H = \log 1/K + \log (x + [H]^+)/(c - [H]^+)$.

The $(p_H)_i$ values derived from the curves are in col. 2 of Table I; col. 1 gives the concentration of the acid; and col. 3 the values of $(p_H)_i$ calculated from $(p_H)_i = 3{\cdot}36 - \frac{1}{2}\log c$ which is the form assumed by the logarithmic equivalent of equation (1) when the values $k_h = 442 \times 10^{-6}$, $k_a = 4{\cdot}5 \times 10^{-6}$, $k_m = 1{\cdot}5 \times 10^{-6}$, and $K = 1{\cdot}85 \times 10^{-5}$ are introduced.

TABLE I.

$(p_H)_i$ values for the *M.V.* mixtures $cCH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$.

c.	$(p_H)_i$ (obs.).	$(p_H)_i$ (calc.).	c.	$(p_H)_i$ (obs.).	$(p_H)_i$ (calc.).
0·01	4·33	4·36	0·20	3·72	3·71
0·05	4·03	4·01	0·50	3·50	3·51
0·10	3·88	3·86	1·00	3·23	3·36

For acetic acid concentrations between 0·01 and 0·5*N*, the agreement between the observed and the calculated $(p_H)_i$ values is within the limits of the experimental errors, and it follows that over this range the hydrogen-ion concentration of the *M.V.* mixture is proportional to the square root of the concentration of the acid. At the highest acid concentration, there is an obvious divergence between the observed and calculated $(p_H)_i$ values. The probable cause of this will be referred to later.

Minimum Velocity and Acid Concentration.

The investigation of the relation between the minimum velocity and the concentration of the acid presents greater difficulties than those which are encountered in the study of the connexion between $[H]_i^+$ and c. The speed of the reaction in the region of the minimum velocity is very small for the smaller concentrations of acetic acid, and it is necessary to pay special attention to the danger of loss of iodine by slow interaction of the latter with the catalysing mixture or by leakage. It is probable that the velocities recorded by Dawson and Carter for the 0·1*N*-acid series in the region of the *M.V.* mixture are abnormally large because the acetic acid used was not quite free from impurities which reacted slowly with the iodine.

For the above reason, new measurements have been made of the minimum velocity, carefully purified acetic acid and sodium acetate being used in the preparation of the mixtures. The mixtures actually employed were those which correspond with the $(p_H)_i$ values recorded in col. 2 of Table I.

The results are summarised in Table II, the numbers in col. 2 representing the measured reaction velocities, whilst those in col. 3 are the velocities calculated from equation (2), which takes the form

$$v_i \times 10^6 = 0{\cdot}383\sqrt{c} + 1{\cdot}5c$$

when the numerical values of k_h, k_a, k_m, and K are inserted. Col. 4 gives the values of $u_i = v_i - k_m c$, col. 5 those of $[H]_i^+$ which correspond with the minima on the v–p_H curves, and col. 6 records the values of $u_i/[H]_i^+$ which, according to equation (3), should be equal to $0{\cdot}88 \times 10^{-3}$. In reference to this ratio, it seems desirable to point out that u_i is not a directly measurable velocity and that

the accuracy with which its value can be obtained depends, not only on the accuracy of the measurement of the minimum velocity v_i, but also on the value assigned to the coefficient k_m. The latter may be derived in various ways, but the methods will not be discussed here. It will suffice to point out that, for the more dilute solutions, the main source of error in u_i lies in the determination of v_i, whilst for the more concentrated solutions the error is in all probability chiefly associated with the value assigned to k_m. In making the comparison between experiment and equation (3), we have actually used the approximate value of $k_m = 1{\cdot}5 \times 10^{-6}$ obtained by the extrapolation method described by Dawson and Carter (*loc. cit.*).

TABLE II.

Values of v_i and $u_i/[H]_i^+$ for $c CH_3{\cdot}CO_2H + x CH_3{\cdot}CO_2Na$.

c.	$v_i \cdot 10^6$ (obs.).	$v_i \cdot 10^6$ (calc.).	$u_i \cdot 10^6$.	$[H]_i^+ \cdot 10^4$.	$u_i/[H]_i^+ \times 10^3$.
0·01	0·056	0·053	0·041	0·0468	0·88
0·05	0·164	0·161	0·089	0·933	0·95
0·10	0·273	0·271	0·123	1·32	0·93
0·20	0·464	0·471	0·164	1·90	0·86
0·50	1·020	1·020	0·270	3·06	0·88
1·00	1·94	1·88	0·44	5·89	0·75

Inspection of Table II shows that for the most part the observed minimum velocities and the values of $u_i/[H]_i^+$ are in satisfactory agreement with the requirements of equations (2) and (3). The data for 1·00N-acetic acid afford the only instance for which the divergence may be definitely regarded as greater than that attributable to errors of experiment.

The divergence led us to investigate in a detailed manner the catalytic effect produced by acid–salt mixtures containing 1N-acid, and the results of these experiments show clearly that at higher salt concentrations there are very considerable differences between the measured velocities and those calculated from the formula $v = k_h[H]^+ + k_a[A]^- + k_m[HA]$. For additions of salt which are not greater than that required to produce the *M.V.* mixture, the differences in question are, however, comparatively small. The observed velocities and those calculated from the above formula are compared in Table III for salt concentrations varying from 0 to 1 g.-mol. per litre.

With regard to the cause of the divergence between the observed and calculated results for 1N-acid solutions, it seems possible that the differences may be connected with the decrease in the ionisation constant of the acid in more concentrated solutions. It is not suggested that the diminution in the ionisation constant is primarily responsible for the observed effects. On the other hand, we are

TABLE III.

Reaction velocities for $1N$-$CH_3 \cdot CO_2H + xN$-$CH_3 \cdot CO_2Na$.

x	0	0·0095	0·019	0·0285	0·038	0·0476	0·0762	
$v \cdot 10^6$ (obs.)	3·40	2·31	1·98	1·94	1·95	1·97	2·15	
$v \cdot 10^6$ (calc.)	3·40	2·33	2·00	1·91	1·88	1·88	1·95	
x	0·0952	0·143	0·190	0·286	0·381	0·500	0·660	1·00
$v \cdot 10^6$ (obs.)	2·25	2·54	2·87	3·52	4·20	4·90*	5·90*	8·05*
$v \cdot 10^6$ (calc.)	1·97	2·15	2·36	2·79	3·21	3·77	4·47	6·01

In the experiments indicated by * iodoform was precipitated.

inclined to attribute the divergences to the formation of catalytically active complex acetate ions, the formation of which, in the more concentrated solutions, is rendered very probable by the fact that acid acetates crystallise out from such solutions (Dukelski, *Z. anorg. Chem.*, 1909, **62**, 114).

The results recorded in Tables I and II justify the conclusion that the catalytic behaviour of acetic acid–acetate mixtures over a wide range of concentration can be quantitatively interpreted in terms of the hypothesis that catalytic effects are produced by and are proportional to the concentrations of the hydrogen ion, the acid anion, and the undissociated acid molecule.

It will now be shown that a knowledge of the minimum reaction velocity and of its variation with the concentration of the acid may be made the basis of methods for determining the values of important constants.

Determination of the Catalytic Activity of the Undissociated Acid from Measurements of Minimum Reaction Velocity.

If the minimum reaction velocities corresponding with the acid concentrations c and c' are denoted by v_i and v_i', then, according to equation (2)

$$v_i - k_m c = 2\sqrt{(k_h - k_m)k_a K c}$$

and

$$v_i' - k_m c' = 2\sqrt{(k_h - k_m)k_a K c'}$$

whence

$$(v_i - k_m c)/(v_i' - k_m c') = \sqrt{c}/\sqrt{c'}$$

or

$$k_m = (v_i/\sqrt{c} - v_i'/\sqrt{c'})/(\sqrt{c} - \sqrt{c'}) \quad . \quad . \quad . \quad (4)$$

The important feature of this equation is that it affords a method for determining the value of the catalytic coefficient k_m for the undissociated acid molecule, which is entirely independent of a knowledge of the constants k_h, k_a, and K. It involves nothing more than a determination of the velocities of reaction for two *M.V.* mixtures the acid concentrations of which are fairly widely separated.

The results obtained for acetic acid by combining the experimental observations for concentrations 0·01 to 0·50N in suitable

pairs are in Table IV. The mean value of k_m thus obtained is $1{\cdot}43 \times 10^{-6}$ and this would suggest that the figure adopted by Dawson and

TABLE IV.

Values of k_m from minimum velocities.

Concentration pairs.	0·1 & 0·01	0·2 & 0·05	0·5 & 0·1	0·2 & 0·01	0·5 & 0·05	0·5 & 0·01
$k_m \cdot 10^6$.	1·41	1·37	1·49	1·38	1·48	1·46

Carter is rather high. For the present it is proposed, however, to retain the approximate value $k_m = 1{\cdot}5 \times 10^{-6}$ as a measure of the catalytic activity of the undissociated acid.

A Kinetic Method for the Determination of Ionisation Constants.

The minimum velocities v_i and v_i' corresponding with acid concentrations c and c' may also be utilised for deriving the value of the dissociation constant of the acid, if this is not too strong. From equation (2) we have

$$(v_i - 2\sqrt{(k_h - k_m)k_aKc})/(v_i' - 2\sqrt{(k_h - k_m)k_aKc'}) = c/c'.$$

Rearranging the terms and squaring, we get

$$(v_i'c - v_ic')^2 = 4(k_h - k_m)k_aK(c\sqrt{c'} - c'\sqrt{c})^2$$

and, since for weak acids, k_m is very small compared with k_h, we obtain

$$K = (v_i'/c' - v_i/c)^2/4k_hk_a(1/\sqrt{c'} - 1/\sqrt{c})^2 \quad . \quad . \quad (5)$$

an equation which gives K in terms of k_h, k_a, and the minimum reaction velocities for two different concentrations of the acid.

The results obtained from the experimental data for acetic acid by combining the same pairs of experiments as were used in the evaluation of k_m are in Table V. The mean value of K is $2{\cdot}16 \times 10^{-5}$. This is considerably greater than the value indicated by the

TABLE V.

Values of K from minimum velocities.

Concentration pairs.	0·01 & 0·1	0·05 & 0·2	0·1 & 0·5	0·01 & 0·2	0·05 & 0·5	0·01 & 0·5
$K \times 10^5$.	2·22	2·30	1·96	2·25	2·06	2·16

conductivity data for acetic acid. In reference to the discrepancy, it may be pointed out that the kinetic method for determining K involves a knowledge of both k_h and k_a, but not of k_m, which is the most difficult of the three coefficients to determine accurately in

the case of acetic acid. To bring the kinetically determined value of K into agreement with the conductivity value, it would be necessary to increase k_h or k_a by 15%, or to alter both these constants so that their product is increased in this proportion. The accuracy with which k_h and k_a can be determined seems to preclude the possibility of any alteration of this magnitude, and there appears to be no obvious explanation of the difference. Until kinetic data for other acids have been obtained, it would appear to be premature to subject the divergence to further discussion.

Experimental.

The measurements of the reaction velocity were made at 25° by the method previously described. The acetone was purified by treatment with sodium iodide, the acetic acid by the action of chromic acid, and the sodium acetate by repeated crystallisation.

Summary.

The minimum velocities of the acetone–iodine reaction under the catalytic influence of mixtures of acetic acid and sodium acetate have been determined for acid concentrations ranging from 0·01 to 1N.

The hydrogen-ion concentration of the minimum-velocity mixture and the magnitude of the minimum reaction velocity vary with the concentration of the acid in accordance with the theoretical predictions.

The ratio of the minimum ionic reaction velocity to the corresponding hydrogen-ion concentration is independent of the concentration of the acid.

It has been shown that minimum velocities may be used for the determination of the catalytic coefficient characteristic of the undissociated acid.

A kinetic method for the determination of dissociation constants of weak acids has been described and applied to the experimental data for acetic acid.

One of us (C. R. H.) desires to thank the Department of Scientific and Industrial Research for a maintenance grant which has enabled him to take part in this work.

The University, Leeds. [*Received, October 27th,* 1926.]

CCCCXXIX.—*The Action of Antimony Trichloride upon Diazotised Diamines.*

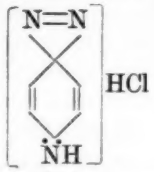
By WILLIAM HERBERT GRAY.

CERTAIN diazonium chlorides were found by May (J., 1912, **101**, 1037) to form insoluble crystalline additive compounds with antimony trichloride. Compounds containing amino- or substituted amino-groups were not investigated. Some of these have now been prepared and found to show two features of interest. They have special properties due to intramolecular condensation between the amino- and the diazo-group; secondly, the whole of the antimony can be removed from them, leaving the organic portion undecomposed. Their small solubility, together with this latter fact, has provided a means of isolating substances such as p-*acetylaminobenzenediazonium chloride* and the *hydrochloride* of the hypothetical *p*-diazoiminobenzene, hitherto undescribed.

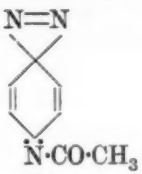
The only salt of *p*-aminodiazobenzene that has been analysed seems to be a chromate, first obtained indirectly by Meldola and Williams (P., 1899, **15**, 196) from *p*-nitrobenzeneazophenol. To this was assigned the formula $NH_2 \cdot C_6H_4 \cdot N_2 \cdot HCrO_4$ (Meldola and Eynon, J., 1905, **87**, 3), although it separated from solution in excess of acetic or sulphuric acid, the presence of a free amino-group under such unlikely conditions being passed over without comment. The same peculiarity is now met with in an antimony trichloride compound and the diazo-compound obtained from it as above. Diazotised acetyl-*p*-phenylenediamine yields with antimony trichloride an almost colourless, crystalline precipitate (see p. 3177) consisting mainly of *di*-(p-*acetylaminobenzenediazonium chloride*)-*antimony trichloride*, $(CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2Cl)_2,SbCl_3$ (I). This is immediately transformed by boiling dilute hydrochloric acid into a bright yellow substance, with an empirical formula corresponding to $NH_2 \cdot C_6H_4 \cdot N_2Cl,SbCl_3$ (II), which crystallises from the excess of acid. Water decomposes this into insoluble basic antimony chlorides and a strongly acid solution, from which is obtained by evaporation a yellow substance with an empirical formula corresponding to $NH_2 \cdot C_6H_4 \cdot N_2Cl$ (III), instead of the expected hydrochloride, $HCl,NH_2 \cdot C_6H_4 \cdot N_2Cl$.

Formula (III) is inadequate: since acidic substituents are absent, it does not explain this lack of salt formation; further, it does not account for the yellow colour. The latter suggests a quinonoid arrangement (IV) such as is given to acyl-*p*-diazoimides (V) by Morgan and his collaborators (compare Morgan and Cleage, J., 1918, **113**, 588; Morgan and Upton, J., 1917, **111**, 195), but it remains

to reconcile this with the pronounced stability of the substance. In the first place the formation in presence of hydrochloric acid is



(IV.)



(V.)

(VI.)

in marked contrast to the immediate reversion to diazonium salt which is effected by this reagent in the cases studied by Morgan. There is, in fact, a certain amount of evidence that in hydrochloric acid solution very little, if any, diazonium salt is present, for solutions in acetic or hydrochloric acid at 100° slowly evolve nitrogen at approximately the same rate, whereas from the following considerations formation of a diazonium salt in the latter should be indicated by a more rapid evolution of nitrogen. Replacement of hydrochloric acid by acetic acid in the case of benzenediazonium chloride is without influence on the decomposition (Cain, *Ber.*, 1905, **38**, 2511), but a diazotised acetic acid solution of acetyl-*p*-phenylenediamine decomposes on heating much more rapidly than a diazotised hydrochloric acid solution (Cain and Nicoll, J., 1902, **81**, 1436). No explanation of this was suggested by Cain; in the light of the present work, it is reasonable to infer that his acetic acid solution contained diazonium salt, and the other, diazoimine salt.

It must be concluded, then, that in the absence of the acyl groups or acidic nuclear substituents which occur in Morgan's compounds, the combined basic influence of the quinonoid imino-group and the group $>C<\begin{matrix}N\\ \|\\ N\end{matrix}$ suffices to permit the formation of a stable diazoimine salt with one molecule of acid. An example of this phenomenon from a different class of compounds has been described by Morgan and Reilly (J., 1914, **105**, 436): 4-Amino-3 : 5-dimethylpyrazole, a diacidic base yielding a dihydrochloride, furnishes after diazotisation only a monohydrochloride. The authors attribute this to the strengthening of one salt-forming centre at the expense of the other —an explanation which appears to cover the case of *p*-diazoiminobenzene also. Willstätter and Mayer (*Ber.*, 1904, **37**, 1494) have shown that the quinonoid imino-group itself is weakly basic; p-*diazoiminobenzene hydrochloride* (IV), on the other hand, is neutral to litmus. Introduction of an acetyl group into this leads to the formation, not of a yellow acetyl compound, that is, the hydrochloride of Morgan's base (V), but of a colourless substance identical with the one obtained by the removal of antimony from (I), namely,

p-*acetylaminobenzenediazonium chloride*, $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2Cl$ (VII).

The stability of (IV) and of p-*diazoiminobenzene hydrochloride–antimony trichloride* (VI) to another change, the loss of diazo-nitrogen, also supports the quinonoid formula. Both remain unchanged for an indefinite period in the solid state (in the dark) and the latter can be repeatedly crystallised from boiling hydrochloric acid. *Di*-(m-*acetylaminobenzenediazonium chloride*)-*antimony trichloride*, $(CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2Cl)_2,SbCl_3$ (VIII), from diazotised acetyl-*m*-phenylenediamine, on the other hand, in which no quinonoid configuration is to be looked for, decomposes spontaneously in a few days to a tar, and immediately on warming with acid; that this is the normal behaviour is seen from benzenediazonium chloride–antimony trichloride, prepared for comparison, which was found to be equally unstable.

Schmidt and Hofmann (*Ber.*, 1926, **59**, 555) attribute the yellow colour of the diazotised aminophenylstibine dichlorides obtained by them to a bridge of residual affinity, $Cl_2Sb \cdot C_6H_4 \cdot N_2Cl$. It is clear that such a formulation is inapplicable to the compounds now under discussion, since the yellow colour persists after removal of the antimony.

Attempts to obtain the free base, *p*-diazoiminobenzene, from (IV) were unsuccessful. Addition of a trace of alkali caused immediate evolution of nitrogen and formation of dark-coloured products; treatment in suspension in non-aqueous media with silver oxide led to similar results, and addition of an aqueous suspension of ferric hydroxide was without effect. The corresponding antimony compound (VI) behaved similarly when treated with alkali, and no substance with the properties of a stibinic acid was obtained from the tarry reaction mixture. The acetylated antimony compound (I), on the other hand, yielded sodium *p*-acetylaminophenylstibinate, thus falling into line with May's compounds (compare D.R.-P. 261825). The considerable stability of the hydrochloride (IV) thus accompanies great instability of the base. Morgan and Micklethwait (J., 1908, **93**, 606) have shown that the stability of diazoimines of the type $C_6H_{5-n}(NO_2)_n \cdot N{:}C_6H_4N_2$ diminishes with n. The least stable member of their series ($n = 0$) was the compound prepared by Ikuta (*Annalen*, 1888, **243**, 282) by the action of sodium hydroxide upon diazotised *p*-aminodiphenylamine, and considered by Hantzsch (*Ber.*, 1902, **35**, 895) to be phenyl-*p*-phenylenediazoimine, $C_6H_5 \cdot N{:}$. Ikuta's compound, however, only gradually decomposed in solution; *p*-diazoiminobenzene, in which acidic

substituents have been entirely removed, is therefore still less stable.

The acetylation of (IV) with acetic anhydride, already mentioned, takes place only in bright sunlight. If concentrated sulphuric acid is added, this is not necessary, but the acetylated product is a sulphur-containing diazonium *compound*, $C_{10}H_{13}O_5N_3S$. This is neutral, but is not a sulphate. Sulphuric acid is, however, slowly set free on boiling with dilute hydrochloric acid. The sulphur is immediately removed by various reagents (p. 3180) with formation of derivatives of *p*-acetylaminodiazobenzene.

Experimental.

The Action of Antimony Trichloride on Diazotised Acetyl-p-*phenylenediamine.*—Acetyl-*p*-phenylenediamine (22·5 g.) was dissolved in a previously warmed mixture of 40% hydrochloric acid (36 c.c.) and water (465 c.c.), and the solution, after decoloration, was rapidly cooled to 12—14° and diazotised during 1 hour with sodium nitrite (10·5 g.) in water (150 c.c.). When diazotisation was carried out below 5°, a considerably poorer yield of antimony compound was obtained. Ice-cold 40% hydrochloric acid in excess (166 c.c.) was then added, followed by a filtered solution of antimony trioxide (19·7 g.) in 40% hydrochloric acid (49 c.c.), with vigorous stirring. A pale brown, crystalline precipitate separated, and was dried on a porous tile in the air until free from hydrochloric acid (yield, 38 g.). By adding the antimony trichloride in several portions, fractions differing in colour could be obtained; the last was very light-coloured, but although homogeneous in appearance, its antimony content and melting point, together with the action of methyl alcohol upon it (see below), showed that it was a mixture of the two compounds (I) and (VI), the former greatly predominating. No separation could be effected by straightforward fractional crystallisation; they were separated as described below. A certain amount of hydrolysis and diazoimine formation evidently occurs during the diazotisation. Sodium hydroxide in slight excess caused a characteristic decomposition with frothing and formation of sodium *p*-acetylaminophenylstibinate.

Di-(p-*acetylaminobenzenediazonium Chloride*)-*Antimony Trichloride* (I).—The pale-coloured fraction (see above) was extracted several times with cold methyl alcohol, which removed bright yellow material, raised the melting point, and lowered the antimony content from 22% to 20%. By a single recrystallisation of the undissolved portion from boiling methyl alcohol, the substance was obtained quite pure in colourless, square plates, m. p. 147° (corr.) (Found: Sb, 19·5; Cl, 28·8. $C_{16}H_{16}O_2N_6Cl_5Sb$ requires Sb, 19·5; Cl, 28·4%).

p-*Acetylaminobenzenediazonium Chloride* (VII).—This was prepared from the foregoing compound by the action of water, or more advantageously from the crude antimony chloride precipitate. In the latter case, the yellow (hydrolysed) impurity could be retained in solution if sufficient alcohol were used in the precipitation. After grinding the crude substance (10 g.) with water (50 c.c.) and filtering, the pale yellow filtrate was treated with alcohol (200 c.c.), kept for a short time to precipitate a small amount of finely-divided solid, and filtered through charcoal. It was then treated with a further 200 c.c. of alcohol and 1370 c.c. of ether; thereafter the compound separated in white, lustrous leaflets, m. p. 131° (corr.), readily soluble in water to a colourless neutral solution, becoming yellow on boiling, with liberation of acetic acid. It is soluble in alcohol, and insoluble in chloroform or cold acetone, the latter giving a deeply coloured solution when warmed. On drying over sulphuric acid at the ordinary temperature the substance retained $\frac{3}{4}$ mol. of water of crystallisation, most of which was lost at 40° in a vacuum over phosphorus pentoxide (Found: N, 20·6; Cl, 17·6; atomic ratio N : Cl = 2·96 : 1. $C_8H_8ON_3Cl$ requires N, 21·3; Cl, 17·95%).

p-*Diazoiminobenzene Hydrochloride–Antimony Trichloride*.—The above crude antimony trichloride precipitate (20 g.) was finely ground and suspended in 10% hydrochloric acid (200 c.c.), heated rapidly to boiling, and boiled for 5 minutes; long, yellow needles then separated from the boiling solution. Yield, 12·4 g.; m. p. 179° (corr.) with sudden decomposition. Use of stronger hydrochloric acid gave a poorer yield. Occasionally the same substance separated in thin, bright yellow plates. It is sparingly soluble in ethyl alcohol or acetic acid, more readily soluble in methyl alcohol or formic acid, from which it crystallises unchanged, readily soluble in aqueous tartaric acid solution, and dissolves with frothing and darkening in sodium hydroxide solution (Found: C, 19·05; H, 1·9; N, 10·9; Cl, 37·1; Sb, 31·8. $C_6H_6N_3Cl_4Sb$ requires C, 18·8; H, 1·6; N, 10·95; Cl, 36·95; Sb, 31·7%).

p-*Diazoiminobenzene Hydrochloride* (IV).—The foregoing antimony compound (16·4 g.) was ground with successive small portions of water (170 c.c. in all) until the water was no longer coloured, and the water-bright extract evaporated at low pressure, the bath being at 60—70°. An orange-coloured paste of small, rectangular plates remained, which was dissolved in warm alcohol (50 c.c.). On cooling, large, yellow, rectangular plates (4·7 g.) separated, m. p. 119° (corr.), still retaining 1 mol. of water even on further recrystallisation from alcohol or precipitation by ether. This water is lost on drying at 60° in a vacuum over phosphorus pentoxide, after which the substance explodes sharply at 155° (corr.). It is extremely soluble

in water to a bright yellow, neutral solution, fairly readily soluble in acetic acid, rather sparingly soluble in alcohol, and insoluble in acetone. Strong daylight decomposes the solid, which becomes black and insoluble in water, but it is stable in the dark. A solution in 10% hydrochloric acid gives an immediate precipitate of large, yellow needles (VI) with antimony trichloride. The aqueous solution remains unchanged at the ordinary temperature for a long period (Found : N, 24·3; Cl, 20·5; atomic ratio N : Cl = 3·0 : 1; atomic ratio after drying, N : Cl = 3·0 : 1. $C_6H_6N_3Cl,H_2O$ requires N, 24·2; Cl, 20·4%). It couples slowly and to a slight extent with R-salt (compare the hydrolysed solution of diazotised acetyl-*p*-phenylenediamine, D.R.-P. 205037, which doubtless contains this substance), but immediately to a chocolate-coloured solid with alkaline β-naphthol. The action of alkali alone led to immediate effervescence and the formation of a black solid, which was not further investigated.

Picrate. By mixing aqueous solutions of the foregoing salt and picric acid, glistening plates were obtained, exploding at 160° (corr.), burning rapidly but quietly on a heated spatula, and remaining unaltered by crystallisation from alcohol. It is sparingly soluble in boiling alcohol or acetone (Found : N, 23·9. $C_{12}H_8O_7N_6$ requires N, 24·1%). The same picrate was obtained from a solution of the antimony compound (VI) in tartaric acid.

Chromate. On the addition of chromic acid to an aqueous solution of the hydrochloride, rectangular plates separated, exploding violently at 160° (corr.), insoluble in alcohol, soluble with darkening in glacial acetic acid. It could be recrystallised from water (Found : Cr, 22·3. $C_6H_7O_4N_3Cr$ requires Cr, 21·9%). The chromate described by Meldola and Eynon (p. 3174) exploded feebly at 144—148° and contained Cr, 21%. The above is doubtless the same substance in a purer state.

Acetylation of p-*diazoiminobenzene hydrochloride.* (a) ***With acetic anhydride.*** No action took place in the cold, in the dark or in diffused light, when *p*-diazoiminobenzene hydrochloride was suspended in acetic anhydride for several weeks, either alone or in presence of pyridine; warming caused decomposition and darkening. When an acetic acid solution was kept with excess of acetic anhydride in the cold, the molecule of water of crystallisation (p. 3178) was removed, but no acetylation took place. If, however, the suspension in acetic anhydride (28 c.c.) was kept in bright sunlight, the solid (5·6 g.) gradually dissolved, a pale brown, clear solution being obtained in about 8 hours. After treatment with charcoal, this was cooled in ice, treated with ice-cold alcohol (28 c.c.), and immediately with 450 c.c. of ether. A small amount of dark oil

was first precipitated, and removed as quickly as possible by repeatedly decanting the solution into fresh flasks. When no more oil separated, the solution was set aside to cool. Colourless needles separated, not depressing the melting point of (VII) (Found: Cl, 17·9. $C_8H_8ON_3Cl$ requires Cl, 17·95%).

(b) *With acetic anhydride and sulphuric acid.* *p*-Diazoiminobenzene hydrochloride (1 g.) was suspended in acetic anhydride (16 c.c.), and concentrated sulphuric acid (0·33 c.c. = 1·1 mols.) added drop by drop. The temperature was allowed to rise slightly. After 15 minutes, the clear, pale red solution was poured into dry ether (65 c.c.) and the crystalline precipitate was thoroughly washed with ether (yield, 1·4 g.) and recrystallised from alcohol–acetic anhydride, from which it separated in lustrous, colourless needles (see p. 3177), m. p. 140° (corr.; decomp.) (Found: C, 41·7; H, 4·8; N, 14·7; S, 11·2. $C_{10}H_{13}O_5N_3S$ requires C, 41·8; H, 4·6; N, 14·6; S, 11·1%). A solution in cold 10% hydrochloric acid gave a white, sulphur-free, crystalline precipitate with antimony trichloride, immediately changed on warming to *p*-diazoiminobenzene hydrochloride–antimony trichloride. It also gave a bright red, sulphur-free azo-compound with β-naphthol. The same sulphur compound was obtained more conveniently from the crude antimony chloride compound of diazotised acetyl-*p*-phenylenediamine in a similar way; 2 mols. of sulphuric acid were here necessary for complete solution, and the ether precipitate was free from antimony.

The following two substances were obtained from it.

p-*Acetylaminobenzenediazonium Chromate.*—The sulphur compound (1·4 g.) was dissolved in water (28 c.c.) and treated with 80% chromic acid solution (0·6 c.c.). Dark yellow prisms (0·9 g.) separated which melted at 136° (corr.) with mild explosion. The substance was free from sulphur (Found: Cr, 18·4. $C_8H_9O_5N_3Cr$ requires Cr, 18·6%).

p-*Acetylaminobenzenediazonium Picrate.*—Solutions of the sulphur compound and picric acid in alcohol were mixed and treated with a little ether. Rosettes of needles quickly separated, m. p., with slight explosion, 146·5° (corr.). The substance was free from sulphur (Found: N, 21·3. $C_{14}H_{10}O_8N_6$ requires N, 21·6%).

Di-(m-*acetylaminobenzenediazonium Chloride*)–*Antimony Trichloride.*—Acetyl-*m*-phenylenediamine hydrochloride, prepared by the method of Wallach and Schulze (*Ber.*, 1882, **15**, 3020), was readily obtained pure by two recrystallisations from water; m. p. 259° (corr.). 3·7 G. of this were dissolved in a mixture of water (47 c.c.) and 40% hydrochloric acid (3 c.c.) and diazotised at 0° during 1 hour with sodium nitrite (1·4 g.). An ice-cold mixture of water (50 c.c.) and 40% hydrochloric acid (28 c.c.) was then added, followed by a

filtered solution of antimony trioxide (3 g.) in 40% hydrochloric acid (7·4 c.c.). The antimony compound separated in yellow platelets, m. p. 94° (corr.) with slight explosion. When treated with water, this gave an amorphous, white precipitate, the suspension giving an immediate deep red colour with R-salt and darkening with frothing on the addition of alkali. Unlike the *p*-acetyl compound, it cannot be crystallised from dilute hydrochloric acid, being at once decomposed on heating, nor dried at 60°, which changes it to a tar. On heating the aqueous suspension, aniline was detected in the steam. For analysis, it was dried on a tile in a desiccator for 2 hours (Found : Sb, 19·5. $C_{16}H_{16}O_2N_6Cl_5Sb$ requires Sb, 19·5%). After several days in the dark at room temperature, it decomposes to a dark, frothing tar.

m-*Acetylaminobenzenediazonium Chromate.*—The foregoing compound (1·25 g.) was ground with several small portions of ice-cold water, and the clarified extract precipitated with cold aqueous chromic acid. Clusters of yellow plates (0·5 g.) separated. After drying in the desiccator, these exploded violently when pressed by a spatula, or even on the addition of cold ammonia solution. In a comparative test, a small quantity of this compound detonated when heated on a spatula and the corresponding *p*-compound (see above) burned rapidly but quietly (Found : Cr, 19·5. $C_8H_9O_5N_3Cr$ requires Cr, 18·6%).

Analytical.—The estimation of antimony in organic compounds by oxidation with permanganate followed by iodometric titration (Fargher and Gray, *J. Pharm. Expt. Ther.*, 1921, **18**, 356; compare Gray, J., 1923, **123**, 641) has now been improved and shortened by the use of oxalic acid to remove the manganese oxides and urea to remove nitrous acid. 0·2 G. of the substance, mixed with powdered potassium permanganate (3 g.), is treated with 50% sulphuric acid (15 c.c.) and then gradually with concentrated sulphuric acid (15 c.c.). The mixture is diluted with water (15 c.c.), boiled gently for 5 minutes, and decolorised with saturated oxalic acid solution. It is then diluted to 120 c.c., urea (1 g.) and potassium iodide (2·5 g.) are added, and the liberated iodine is determined by thiosulphate after 15 minutes' standing. Towards the end, the liquid should again be diluted considerably with water; the yellow colour, not due to iodine, which otherwise persists past the end-point, is thus destroyed.

Chlorine. After a number of methods had been tried for the determination of chlorine in presence of antimony in these compounds, the following was found to be the only practicable one. The substance (0·2 g.) is mixed with a little water and potassium permanganate (1 g.) in a small flask containing a tube of concentrated sulphuric acid. The

flask is then connected to absorption bulbs containing potassium iodide solution, the tube of sulphuric acid emptied by tilting, and the flask heated until all the chlorine has been evolved. A small correction, found from a control experiment on a substance of known chlorine content, is applied.

The author wishes to thank Dr. T. A. Henry for the kind interest he has taken in the work, and also Mr. A. Lovecy for help in the preparation and analysis of the products described.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON. [*Received, October 1st*, 1926.]

CCCCXXX.—*Low Temperature Oxidation at Charcoal Surfaces. Part III. The Behaviour of Blood Charcoal and the Influence of Temperature on the Reaction Rate.*

By ERIC KEIGHTLEY RIDEAL and WINIFRED MARY WRIGHT.

IN previous communications (J., 1925, **127**, 1347; this vol., p. 1813) it was shown that charcoals containing both iron and nitrogen were catalytically active for the oxidation of oxalic acid, and that the surface of the charcoal was by no means uniform but could, by the method of selective poisoning, be divided into areas of different specific catalytic activities. Reasons were given for the assumption that two of the areas of high catalytic activity were promoted areas, *i.e.*, characterised by their chemical composition; thus, the specific activity in the oxidation of oxalic acid of a surface of an iron–carbon–nitrogen complex was about 800 and that of an iron–carbon complex about 50 times that of the catalytically active portion of the charcoal.

Since blood charcoal has been employed for a number of diverse purposes, it seemed desirable to examine this material by the method of selective poisoning and thus to ascertain the nature and extents of the patches of various specific activities.

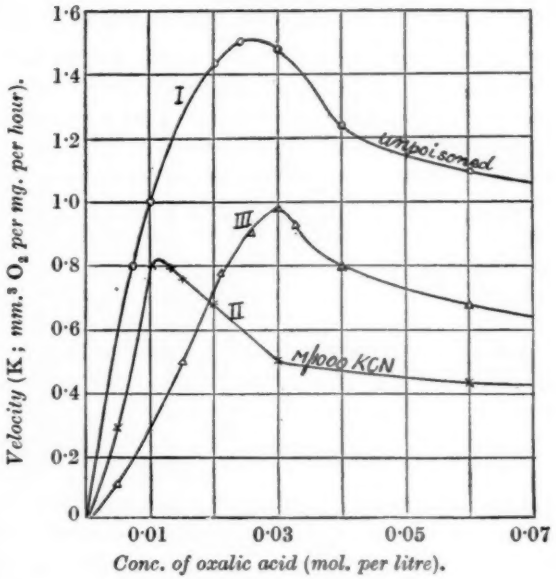
EXPERIMENTAL.

Merck's blood charcoal was employed after purification by treatment with hydrochloric acid and heating for 2 hours in a silica crucible at low red heat. (Analysis showed Fe, 0·037; N, 7·0; and 0·80% of salts of calcium and sodium.) Its specific surface was found, by the saturation method with methylene-blue, to be 210 sq. m. per g.—some eight times that of the pure sugar charcoal

previously investigated. The rates of autoxidation and of oxidation of oxalic acid of various concentrations in the presence of poisons such as amyl alcohol and acidic potassium cyanide were studied with the aid of a Barcroft differential shaking manometer as described in Parts I and II. In every case, 100 mg. of charcoal were allowed to come to equilibrium with the oxalic acid solutions of various concentrations by agitation and separation in a centrifuge. To these solutions known amounts of amyl alcohol were added, the solutions agitated in the differential manometer, and the rate of

FIG. 1.

Blood charcoal.



oxygen uptake measured. The bulk concentration of the alcohol was measured by the drop-weight method, and hence the amount adsorbed was calculated.

The autoxidisable area of blood charcoal was almost inappreciable and, although varying from sample to sample, did not exceed in any one case 0·03% of the total surface, the average rate of oxygen uptake at 40° being 0·008 mm.³ per mg. per hour. The maximum rate of oxidation of oxalic acid occurred in 0·025*M*-solution, as is evident from Curve I (Fig. 1).

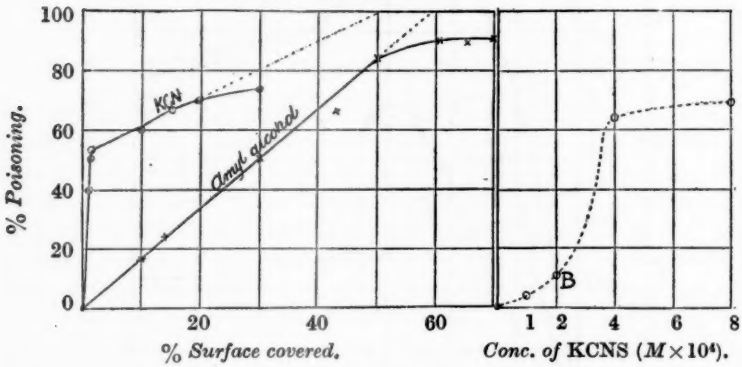
On poisoning with amyl alcohol, a linear curve (see Fig. 2) was obtained up to 80% inhibition, beyond which no further poisoning occurred owing to limitations imposed by the sparing solubility of

the alcohol. By extrapolation in the manner already described (Part I), the fraction of the total surface catalytically active was found to be 55%, a value to be compared with the following: sugar charcoal 40·5%, nitrogen–sugar charcoal 52%, iron–sugar charcoal 44%, iron–carbon–nitrogen charcoal 30%.* Blood charcoal thus possesses a relatively large specific surface, and a large fraction of the total surface is capable of catalytically accelerating the oxidation of oxalic acid.

The poisoning with cyanide was determined as follows: In each experiment a suspension of 100 mg. of charcoal in 0·02M-oxalic acid was employed and various concentrations of potassium cyanide with an equivalent of hydrochloric acid were added. The adsorption of the cyanide was determined from the bulk concentration at equilibrium

FIG. 2. FIG. 3.

Blood charcoal and oxalic acid.



as estimated by silver titration employing the electrometric method. The rate of oxygen uptake and its diminution with the increase in surface covered by the cyanide were determined with the aid of the differential manometer.

Only one well-defined break in the surface covered–velocity curve was obtained (Fig. 2). The marked break in the curve occurs at a point where only 1·2% of the total surface is covered, and thus 1·2% of the total surface is responsible for 54% of the total catalytic activity of the charcoal. This very active portion was poisoned

* Kubota and Yoshikawa (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1925, 3, 223) have shown that a reduced-nickel catalyst has three distinct catalytically active areas each of which can be completely and selectively poisoned. Although the total area may vary with the mode of treatment of the catalyst, they claim that the ratios of the areas remain unchanged. A critical examination of their data, however, does not lead us to an unqualified acceptance of this view.

by $M/1000$-potassium cyanide and the maximum velocity of oxygen uptake on the remainder of the charcoal occurred with an oxalic acid concentration of $0{\cdot}01M$ (Curve II, Fig. 1) comparable with that for sugar charcoal, *i.e.*, $0{\cdot}0075M$. At this concentration the reaction velocity was $k = 0{\cdot}81$ mm.^{3} of oxygen per mg. of charcoal per hour. From the velocity–concentration curves for the unpoisoned and the partially poisoned charcoal the reaction velocity maximum (see Curve III, Fig. 1) for the more active surface was found to be $k = 0{\cdot}98$ mm.^{3} of oxygen per mg. per hour. Since the total surface of the charcoal is 210 sq. m. per g. and 1·2% of this is the very active iron–carbon surface, the specific activity of this surface is accordingly $0{\cdot}98/(210 \times 10^4 \times 0{\cdot}012) = 39 \times 10^{-6}$ c.c. of oxygen per sq. cm. per hour. In a similar manner, the specific activity of the less active area is found to be $0{\cdot}76 \times 10^{-6}$ in the same units. When these values are compared with the specific activities of the three active patches obtained in the synthetic charcoals (for the C–C, $k = 0{\cdot}70 \times 10^{-6}$; for the Fe–C, $k = 40 \times 10^{-6}$; and for the Fe–C–N, $k = 770 \times 10^{-6}$), it would appear that blood charcoal contains but two active patches—one of 1·2% of the total area possessing an activity comparable with that of the synthetic Fe–C complex, and the other corresponding to unpromoted active carbon. It is somewhat remarkable that no sign of an iron–nitrogen–carbon complex is observed in the curves in spite of the fact that this charcoal contains not less than 7% of nitrogen.

The Range of Influence of the Iron Promoter.—The dispersion of the iron in the blood charcoal must be fairly uniform and we may regard the charcoal as an intimate mixture of carbon and iron atoms in the ratio of 12,000 : 1. With such a bulk distribution the surface distribution will be of the order of $(12{,}000)^{2/3} : 1$ or 536 : 1. On the assumption that every iron atom in the surface is active in promotion, and since the active area is 1·2% of the total surface, one atom of iron renders $536 \times 1{\cdot}2/100 = 6{\cdot}4$ (or, say, 6) atoms of carbon active, both for the selective adsorption of cyanides and for the catalytic oxidation of oxalic acid. The existence of an iron atom in the centre of a benzene ring or with six co-ordinated carbon atoms, comparable with its complex cyanide ions, would offer a simple interpretation of this remarkable result.

Attempts to achieve such a high carbon : iron ratio for the active patches in synthetic charcoals did not succeed, and it appeared likely that uniform dispersion of the iron could not be readily obtained when incorporated as a simple iron salt in a mixture undergoing carbonisation.

The Temperature Coefficients of the Reactions on the Active Surfaces.

In homogeneous gas reactions it is possible to calculate the energy of activation from the temperature coefficient. Certain limitations are imposed in dealing with heterogeneous actions. Before such calculations can be made it is necessary to be certain that we are dealing with identical concentrations of the reactant over the temperature range examined. In the case under consideration, this involves the assumption that the areas and natures of the active patches, as well as the adsorption of the reactants, remain unchanged or, if any changes occur, that these can be determined so that the necessary corrections can be applied.

Sugar Charcoal.—In Part I the temperature coefficient of the autoxidation of sugar charcoal was found to be $k_{50}/k_{40} = 1{\cdot}80$, and the reaction was independent of the oxygen pressure over wide ranges. On the assumption that the area and nature of an active patch over the temperature range examined remain constant, the concentration of reacting adsorbed oxygen–carbon complex is likewise constant, and the temperature coefficient can thus be utilised for determination of the energy of activation. By application of the Arrhenius equation $\log_e k_{50}/k_{40} = -E(1/T_2 - 1/T_1)/R$ we obtain a value of $E = 11{,}800$ cals. for the energy of activation for autoxidation. In the oxidation of oxalic acid both reactants are adsorbed; thus on either side of the point of maximum velocity the reactant adsorbed in excess acts as an inhibitor to the reaction. The temperature coefficient will therefore vary with the concentration of oxalic acid. The coefficient of adsorption of oxalic acid within the temperature range 30—40° is small and negative, being $3{\cdot}74 \times 10^{-7}$ mol. per mg. at 30° and $3{\cdot}70 \times 10^{-7}$ at 40°; that for the oxygen is unknown, although the solubility in the liquid falls from 0·0267 to 0·0233. We should anticipate that the temperature coefficient would steadily rise as we increase the oxalic acid concentration. This anticipation is verified by the following figures.

k_{40}/k_{30}	2·00	2·03	2·06
Molarity of oxalic acid	0·005	0·01 (optimum)	0·1

The correction to be applied for the change in adsorption with change in temperature thus appears to be relatively small, and on the assumption that the extent and nature of the active area remain unchanged we may determine the energy of activation for the sugar-charcoal complex from the temperature coefficient at the optimum, *viz.*, 2·03. This yields a value of $E = 14{,}020$ cals. per g.-mol. The validity of this value is based upon the hypothesis that oxalic acid and oxygen are both actually adsorbed on the active area. That oxalic acid is adsorbed could be demonstrated by the

fact that on poisoning with amyl alcohol oxalic acid is displaced from the surface. In each experiment 100 mg. of charcoal were shaken with 10 c.c. of oxalic acid solutions of various concentrations. When adsorptive equilibrium was attained, the oxalic acid in solution was determined by titration with permanganate. Sufficient amyl alcohol was added to arrest catalytic oxidation and the bulk concentration of oxalic acid was again determined; calculation then gave the amount of acid displaced by the alcohol from the active patch, of which the area was 34·5% of the total area of 10·8 sq. m. per g., as determined by the methylene-blue method. The following table shows the results, from which it will be seen that oxalic acid is preferentially adsorbed on the catalytically active area, but even before the maximum velocity is attained this solute is likewise partly adsorbed on the inactive area.

Bulk conc. of oxalic acid.	Quantity adsorbed (g.-mols. per mg.) $\times 10^7$.	Quantity displaced by amyl alcohol on poisoning (g.-mols. per mg.) $\times 10^7$.	Quantity left on inactive portion (g.-mols. per mg.) $\times 10^7$.
0·0025*M*	0·5	0·5	0
0·005*M*	0·92	0·91	0·01
0·01*M* (optimum rate)	1·45	1·1	0·35
0·02*M*	2·1	1·8	0·30
0·04*M*	3·8	2·6	1·2

Blood Charcoal.—At the maximum (Curve I, Fig. 1) with 0·025*M*-oxalic acid the temperature coefficient was $k_{40}/k_{30} = 1·97$ (mean of six determinations). When the charcoal was poisoned by the addition of *M*/1000-potassium cyanide, the velocity at the new maximum at 0·01*M* (Curve II, Fig. 1) was 54% of its original value. The addition of *M*/500- and *M*/200-potassium cyanide did not reduce this velocity appreciably. It may therefore be assumed that 46% of the velocity is due to the iron-containing area. The temperature coefficient of this partially poisoned charcoal was 2·01, comparable with the value 2·03 found for the sugar charcoal.

If x be the coefficient of the iron-containing area, we thus obtain $2·01 \times 0·54 + 0·46x = 1·97$, whence $x = 1·92$. This is appreciably smaller than the temperature coefficient for the unpromoted area (2·03), and the corresponding value for the energy of activation is 12,900 cals.

A few experiments were likewise carried out with a charcoal prepared from Bismarck brown containing iron impurities (see Warburg, *Biochem. Z.*, 1924, **165**, 461). It resembled that prepared from urea, sugar, and ferric chloride in its high velocity of oxidation of oxalic acid and in its behaviour towards the poisons, cyanides and thiocyanates; it may therefore be assumed that it contains the three groups C–C, Fe–C, and Fe–C–N. The temperature

coefficient of the unpoisoned charcoal at the maximum was 1·91. On the addition of potassium thiocyanate the velocity fell, and the temperature coefficient rose as follows :

Conc. of KCNS.	k_{40}.	% Poisoning.	k_{40}/k_{30}.
0	6·60	0	1·91
$M/10{,}000$	6·28	4·9	1·91
$M/5{,}000$	5·94	10·0	1·92
$M/2{,}500$	2·34	64·5	1·93
$M/1{,}250$	2·03	69·3	1·94

Sufficient charcoal was not available to determine the adsorption of the thiocyanate. As a rough approximation, the curve obtained by plotting bulk concentration against percentage poisoning (Fig. 3) suggests that there are three areas on this charcoal corresponding to those on urea–iron–sugar charcoal, and that about 15% of total activity is due to the Fe–C, 55% to the Fe–C–N, and 30% to the C–C areas (compare Part II). Then, substituting the values already obtained for the temperature coefficients for the C–C and Fe–C areas, that for Fe–C–N (X) is given by the equation $1{\cdot}92 \times 0{\cdot}15 + X \times 0{\cdot}55 + 2{\cdot}03 \times 0{\cdot}30 = 1{\cdot}92$, or $X = 1{\cdot}86$. This value can be confirmed more directly by the following method. Taking the point B (Fig. 3) of the partially poisoned charcoal, then, of the remaining activity, 65% is due to the Fe–C–N area and 35% to the C–C area; hence $0{\cdot}65X + 2{\cdot}03 \times 0{\cdot}35 = 1{\cdot}91$, or $X = 1{\cdot}86$. Taking X as 1·86, the energy of activation $E = 12{,}290$ cals.

We thus obtain for the energies of activation as determined from the temperature coefficients within the range 30—40°, for the C–C complex, 14,020; for the Fe–C complex, 12,900; and for the Fe–C–N complex, 12,290 cals. Whilst these critical increments are in the order anticipated inasmuch as the velocity of oxidation per sq. cm. rises with falling critical increment, yet they do not show the exponential relationship to the reaction velocities which is to be anticipated if the actual surface concentrations and arrangements of the molecules are identical, and if the complexes thus formed differ only in stability as was originally indicated (Part I).

It is probable that the nature of the surface adsorption of the oxygen is more important than the surface concentration of the oxalic acid; for, on comparison of the properties of the corresponding active areas (C–C) of sugar and blood charcoal, we find that, whereas they yield identical velocities for the oxidation of oxalic acid at the optimum concentrations ($0{\cdot}70$ and $0{\cdot}76 \times 10^{-6}$ c.c. of oxygen per sq. cm. per hour) and almost identical temperature coefficients ($k_{40}/k_{30} = 2{\cdot}01$ and 2·03), yet the adsorption of oxalic acid differs markedly on the two surfaces.

The differences in the adsorbing properties of the catalytically

active charcoal areas of blood charcoal and pure sugar charcoal may be tabulated thus :

	Charcoal.	
	Blood.	Sugar.
Conc. of oxalic acid for optimum rate	0·025*M*	0·01*M*
Adsorption of oxalic acid per sq. cm. of active area at optimum conc. (molecules)	$3{\cdot}12 \times 10^{14}$	$17{\cdot}9 \times 10^{14}$
Conc. of amyl alcohol to effect poisoning	0·023*M*	0·007*M*
Adsorption of amyl alcohol per mg. (g.-mol.)	$4{\cdot}22 \times 10^{-7}$	$1{\cdot}58 \times 10^{-7}$
Adsorption of amyl alcohol per sq. cm. of total surface	$1{\cdot}27 \times 10^{14}$	$8{\cdot}9 \times 10^{14}$
Adsorption of amyl alcohol per sq. cm. of active surface	$23{\cdot}3 \times 10^{14}$	$23{\cdot}3 \times 10^{14}$

Although these actual concentrations are based upon the hypothesis that one amyl alcohol molecule is attached to one carbon atom, a view which is open to criticism, yet the differences in the relative adsorptions indicate clearly that the two areas are not identical in all respects. These data incline us to the view that the process of the chemical reaction involves activation of the oxygen rather than of the acid. The catalytically active area is thus that portion of the charcoal surface which permits of excitation of adsorbed oxygen to a level at which it can react with oxalic acid. It seems probable that the area of a carbon surface which is catalytically active will vary with the nature of the substance undergoing oxidation; substances not readily oxidised may only undergo oxidation on a very restricted area on which the oxygen can readily be excited or activated to a relatively high potential. Such substances, which hitherto we have found to be characterised only by the possession of two polar groups, may also be defined by possessing different oxidation potentials, all of which are, however, below a certain critical value as determined by their powers of anodic depolarisation. We hope to inquire into the relationship between the rates of oxidation of such substances, the areas available for such oxidations, and the powers of anodic depolarisation which these substances may possess.

Summary.

The natures of the surfaces of blood charcoal have been examined by the methods previously detailed (J., 1925, **127**, 1347; this vol., p. 1813). Only two active areas were identified—one corresponding to the Fe–C complex, and one to the C–C complex of synthetic charcoals.

The area of carbon surface active for the oxidation of oxalic acid varies within the limits 30—55% of the total, depending on the method of preparation of the charcoal. The range of promoter action of one iron atom is found to extend to not more than six carbon atoms, and an analogy is sought in the complex iron cyanides.

The temperature coefficients of autoxidation and of oxidation of oxalic acid on the various active patches are determined. It is shown that the variation in adsorption of oxalic acid with the temperature is small; the variation in the temperature coefficient of oxidation with the concentration of oxalic acid is shown to follow the course anticipated. The distribution of oxalic acid between the active and inactive areas for various concentrations is determined. From the temperature coefficients, the following critical energy increments per g.-mol. are calculated: for autoxidation, 11,800 cals.; for oxidation of oxalic acid on the C–C complex, 14,020 cals.; on the Fe–C complex, 12,900 cals.; and on the Fe–C–N complex, 12,290 cals.

Whilst corresponding surfaces on a sugar and blood charcoal are identical in respect of the rates of oxidation of oxalic acid and the temperature coefficients of the rates, yet they differ in the amount of oxalic acid adsorbed per sq. cm. at the concentrations of maximum velocity. Stress is laid upon the importance of investigating the properties of adsorbed oxygen in more detail, and a relationship is suggested between the area of surface catalytically active, the velocity, and the depolarising potential of the substance undergoing oxidation.

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[*Received, October 9th*, 1926.]

CCCCXXXI.—*A Phase-rule Study of the Zinci-, Cadmi-, Mercuri-, and Nickelo-cyanides of Potassium.*

By ALEXANDER STEVEN CORBET.

As several points of interest arose in a previous investigation on the cupro-, argento-, auro-, and thallo-cyanides of potassium (Bassett and Corbet, J., 1924, **125**, 1660) it appeared probable that other groups of complex cyanides would repay examination. The cyanides of zinc, cadmium, mercury, and nickel are closely allied; all form complex cyanides of the type $K_2M''(CN)_4$, whilst some give sodium salts $Na_2M''(CN)_4$ or $NaM''(CN)_3$ or both. Although previous investigations have been chiefly of a preparative or an analytical nature, the subject has also been studied from other aspects: thus, the electrical conductivities of aqueous solutions of the potassium salts under consideration have been determined at 25° by Walden (*Z. anorg. Chem.*, 1900, **23**, 373), and further electrolytic work has been carried out by Brochet and Petit (*Ann. Chim.*, 1904, **3**, 449) and by Kunschert (*Z. Elektrochem.*, 1905, **11**,

348). The chief interest in these compounds, however, lies in their use in qualitative and quantitative analysis, and a phase-rule study of the three-component systems, $KCN–Zn(CN)_2–H_2O$, etc., has afforded much information as to the conditions underlying their formation.

The System Potassium Cyanide–Zinc Cyanide–Water.

By crystallisation of a solution of zinc cyanide in aqueous potassium cyanide Rammelsberg (*Pogg. Ann.*, 1836, **38**, 364) obtained the salt $K_2Zn(CN)_4$ as colourless, octahedral crystals. This compound was investigated in more detail by Haidlen and Fresenius (*Annalen*, 1842, **43**, 129), Gmelin ("Handbook of Chemistry," 1852, VII, 424), Berthelot (*Compt. rend.*, 1899, **128**, 706), Loebe (Diss., Berlin, 1902), and Sharwood (*J. Amer. Chem. Soc.*, 1903, **25**, 570). A thermal investigation of the binary system $KCN–Zn(CN)_2$ by Truthe (Diss., Göttingen, 1912) gave no indication of complex cyanides other than the dipotassium salt.

Of the sodium zincicyanides, Rammelsberg (*Pogg. Ann.*, 1837, **42**, 114) prepared $NaZn(CN)_3,2\frac{1}{2}H_2O$ as glistening, white plates, and subsequently Loebe (*loc. cit.*) and Sharwood (*loc. cit.*) confirmed the existence of a monosodium salt, which was, however, decomposed by water with separation of a basic zinc cyanide. Although unable to obtain the monosodium salt, Herz (*J. Amer. Chem. Soc.*, 1914, **36**, 912) prepared a disodium compound, $Na_2Zn(CN)_4,3H_2O$, as efflorescent, orthorhombic crystals by crystallisation of a solution of zinc cyanide in aqueous sodium cyanide.

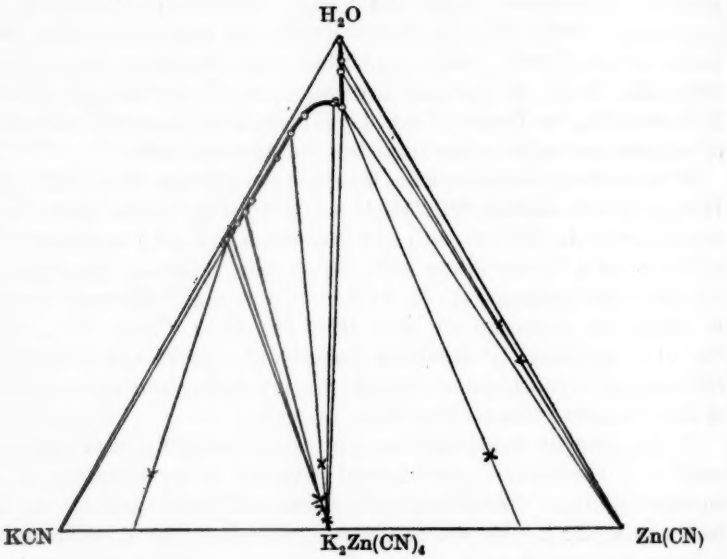
In the present investigation, the salt $K_2Zn(CN)_4$ was obtained readily as transparent, octahedral crystals by evaporation of an aqueous solution containing potassium and zinc cyanides in the molar ratio 2 : 1. By an analogous procedure the corresponding sodium compound was prepared admixed with a little sodium cyanide [Found : NaCN, 37·8; $Zn(CN)_2$, 41·1. $Na_2Zn(CN)_4,3H_2O$ requires NaCN, 36·4; $Zn(CN)_2$, 43·6%]. Thus prepared, the crystals were of indeterminate shape and stable in air. On application of pressure, however, they melted to a clear liquid from which transparent, hexagonal plates separated on evaporation. The transition point between this substance and a lower hydrate or the anhydrous salt was found to be *ca.* 52°.

In an endeavour to prepare the monosodium compound, excess of zinc cyanide was added to a 10% solution of sodium cyanide and maintained at a temperature just below the b. p. for an hour; the undissolved zinc cyanide was removed and the solution concentrated. The crystals which separated appeared to contain the mono- and di-sodium salts in the ratio 3 : 7 [Found : NaCN, 31·27;

$Zn(CN)_2$, 44·27%, corresponding to 1·67 NaCN, $Zn(CN)_2$, 3·57 H_2O], and gave a white turbidity on addition of water, confirming Sharwood's observations concerning the mono-salt. An attempt to prepare a monopotassium compound by a corresponding method yielded the salt $K_2Zn(CN)_4$.

The complex potassium zincicyanide was completely decomposed by 0·1*N*-sulphuric acid and hence it was possible to estimate the cyanogen group volumetrically: excess of acid was added to the solution and, after standing over-night, this excess was determined by titration with 0·1*N*-sodium hydroxide and methyl-orange.

FIG. 1.



An examination of the three-component system KCN–$Zn(CN)_2$–H_2O was carried out at 25° and the results are given in Table I and Fig. 1. No indication was obtained of a complex cyanide other than the well-known potassium salt. The diagram bears a striking resemblance to that representing the corresponding gold cyanide system (J., 1924, **125**, 1663), particularly in that solutions containing 20—41% of potassium cyanide contain less than 1% of zinc cyanide; the maximum solubility of the latter occurs in a solution in which the respective cyanides are present in approximately the ratio required to form the double salt. It may be seen from the figure that the solubility curve of zinc cyanide does not completely coincide with a line representing the ratio of potassium cyanide to zinc cyanide necessary to form the compound $K_2Zn(CN)_4$. This indicates

that zinc cyanide is slightly soluble in a solution of potassium zincicyanide, a fact which is of importance in the cyanometric estimation of zinc (Treadwell, *Chem.-Ztg.*, 1914, **38**, 1230). By a volumetric method, depending on addition of a zinc solution to potassium cyanide until a permanent turbidity is produced, high values may be obtained, whilst low values may result if the reverse procedure is adopted. In both methods, however, the concentration of potassium cyanide is important, a 0·2*N*-solution being preferable to a 0·5*N*-solution, although Treadwell states that uncertain values may be obtained in very dilute solutions.

TABLE I.

The System $KCN–Zn(CN)_2–H_2O$ *at* 25°.

Liquid phase.		"Rest."		
% KCN.	% $Zn(CN)_2$.	% KCN.	% $Zn(CN)_2$.	Comp. of solid phase.
41·7	0·00	—	—	KCN.
41·15	Trace	77·79	10·13	KCN + $K_2Zn(CN)_4$.
39·04	Trace	51·59	44·24	
37·15	0·12	—	—	
34·46	0·17	51·72	43·06	
32·65	0·20	—	—	
23·56	0·67	46·69	45·95	$K_2Zn(CN)_4$.
18·22	0·47	47·60	39·48	
14·17	1·50	—	—	
7·65	5·75	—	—	
6·64	5·86	53·04	45·90	
6·77	6·97	16·09	68·19	$K_2Zn(CN)_4$ + $Zn(CN)_2$.
3·81	3·33	1·98	56·45	
2·50	2·30	1·52	63·93	$Zn(CN)_2$.
Trace	Trace	Trace	76·87	

The System Potassium Cyanide–Cadmium Cyanide–Water.

Rammelsberg (*Pogg. Ann.*, 1836, **38**, 364) described the preparation and properties of cadmium cyanide and of the dipotassium salt, $K_2Cd(CN)_4$, but later Joannis (*Compt. rend.*, 1881, **93**, 272; *Ann. Chim.*, 1882, **26**, 482) stated that the cyanide or a basic cyanide, $2Cd(CN)_2,CdO,5H_2O$, may be obtained according to the method of preparation. By mixing concentrated solutions of potassium cyanide and cadmium sulphate, and washing the adhering potassium sulphate from the precipitate, Joannis obtained the cyanide $Cd(CN)_2$ as a white, crystalline powder. Loebe (*loc. cit.*), whilst confirming the constitution of Joannis's basic compound, formulated a new substance as $3Cd(CN)_2,CdO,16H_2O$.

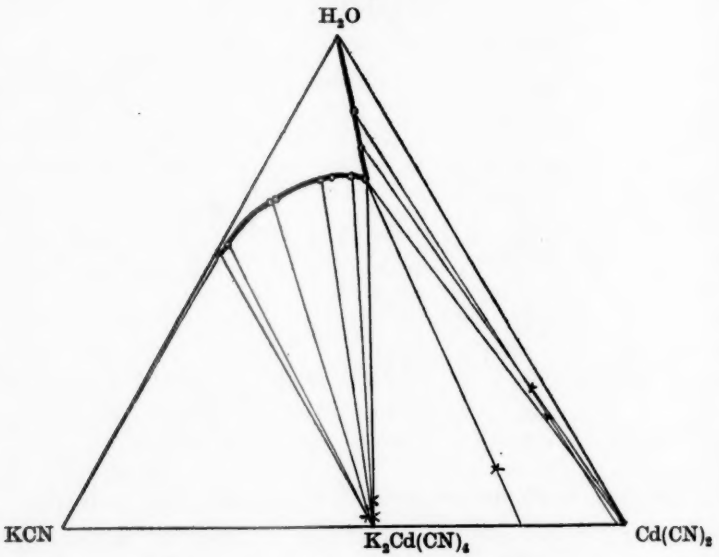
An unsuccessful attempt was made to prepare cadmium cyanide by Joannis's method. Very little precipitation occurred at room temperature and the product contained large and variable amounts of sulphate which could not be removed by washing. On boiling

the freshly-precipitated solution a product richer in cadmium was precipitated but complete removal of sulphate was not accomplished. Employment of more dilute solutions did not yield very different results. That this behaviour may be attributed to some complex formation seems probable, for no immediate precipitation occurred on addition of cadmium sulphate to a solution of potassium cadmicyanide. On the other hand, by using cadmium nitrate, a white, amorphous powder, having the constitution

$$3Cd(CN)_2,CdO,4H_2O$$

and corresponding to Loebe's basic cyanide, was obtained.

FIG. 2.



Potassium cadmicyanide was readily prepared and its properties corresponded with those described by Haidlen and Fresenius, Gmelin, and Loebe. In addition to a sodium salt, $NaCd(CN)_3,1\frac{1}{2}H_2O$, Loebe prepared cadmicyanides of the alkaline-earth metals.

The results obtained in a phase-rule study of the system $KCN–Cd(CN)_2–H_2O$ at 25° are given in Table II and plotted in Fig. 2. This system differs from any previously examined in that solutions of the double salt are capable of dissolving appreciable amounts of the cadmium cyanide. As in the zinc cyanide system the extended range of existence of the double salt indicates that it may be prepared readily, a solution of the simple cyanides in almost any ratio depositing pure crystals of the cadmicyanide on evaporation.

TABLE II.

The System KCN–$Cd(CN)_2$–H_2O *at* 25°.

Liquid phase.		"Rest."		
% KCN.	% $Cd(CN)_2$.	% KCN.	% $Cd(CN)_2$.	Comp. of solid phase.
41·7	0·00	—	—	KCN.
40·67	0·82	44·18	53·63	$K_2Cd(CN)_4$.
28·62	4·65	43·23	55·61	
28·22	4·54	43·55	56·04	
17·79	10·70	43·11	54·56	
15·16	12·53	41·28	53·99	
11·65	16·15	43·35	49·81	
9·47	19·14	16·68	71·26	$K_2Cd(CN)_4$ + $Cd(CN)_2$.
* 7·82	15·73	2·07	69·48	$Cd(CN)_2$.
* 4·68	10·21	2·55	75·27	
* Trace	0·38	—	—	
* Trace	0·36	—	—	

* The solid phase in these cases was undoubtedly a basic cadmium cyanide, but the error introduced is not serious.

The System Potassium Cyanide–Mercuric Cyanide–Water.

The solubility of mercuric cyanide in water and the density of aqueous solutions of the salt have been the subject of numerous investigations. When plotted, however, the results obtained for the solubility determinations at various temperatures do not fall on a smooth curve. Mercuric cyanide readily forms double crystalline compounds with many metallic salts and, of these, a large number have been described. By crystallisation of a solution of mercuric cyanide in aqueous potassium cyanide, Rammelsberg (*Pogg. Ann.*, 1836, **38**, 364) obtained potassium mercuricyanide as transparent, octahedral crystals and showed its constitution to be $K_2Hg(CN)_4$. In addition to the sodium compound, $NaHg(CN)_3$, other mercuricyanides of various types have been prepared by Grossmann and Forst (*Ber.*, 1904, **37**, 4141).

The results of a phase-rule examination of the system KCN–$Hg(CN)_2$–H_2O at 25° are given in Table III and plotted in Fig. 3. As in the two previous systems, the range of existence of solid potassium cyanide in contact with solutions containing the double salt is very limited. The increased solubility of potassium mercuricyanide in presence of mercuric cyanide and *vice versa* is, however, the most striking feature of the diagram.

The System Potassium Cyanide–Nickel Cyanide–Water.

Potassium nickelocyanide, $K_2Ni(CN)_4,H_2O$, was obtained as reddish-yellow, rhombic prisms by Rammelsberg (*loc. cit.*) by crystallisation of an aqueous solution of potassium cyanide containing nickel cyanide. The compound was examined further by

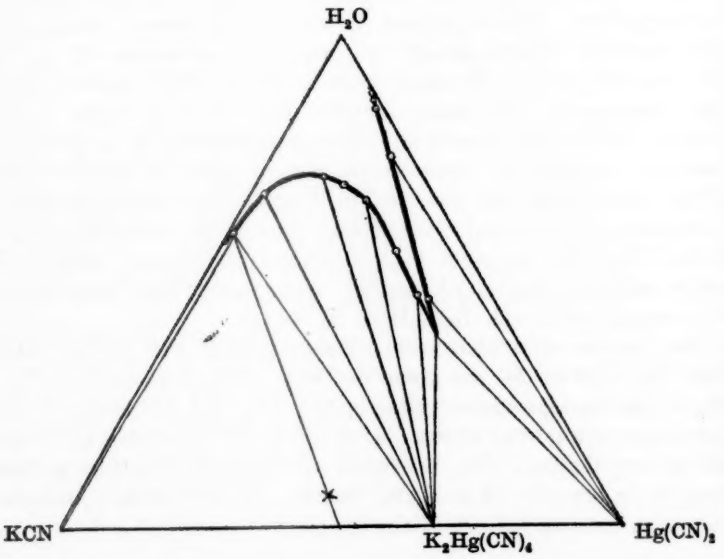
TABLE III.

The System $KCN–Hg(CN)_2–H_2O$ *at* 25°.

Liquid phase.		"Rest."		Comp. of solid phase.
% KCN.	% $Hg(CN)_2$.	% KCN.	% $Hg(CN)_2$.	
41·7	0·00	—	—	KCN.
39·71	0·49	49·17	44·82	KCN + $K_2Hg(CN)_4$.
29·47	2·34	34·59	63·07	
17·34	11·09	32·79	63·54	
14·54	15·54	31·42	64·01	
12·54	20·65	32·81	62·97	$K_2Hg(CN)_4$.
12·51	31·19	33·62	64·16	
12·81	39·96	33·87	65·86	
11·37	41·85	0·81	98·02	
3·97	20·34	0·48	98·00	
* 1·09	13·53	—	—	
* 0·56	11·83	—	—	$Hg(CN)_2$.
* 0·28	10·89	—	—	
* 0·00	10·00	—	—	
0·00	10·00	0·00	81·33	

* Sherrill, *Z. physikal. Chem.*, 1903, **43**, 719.

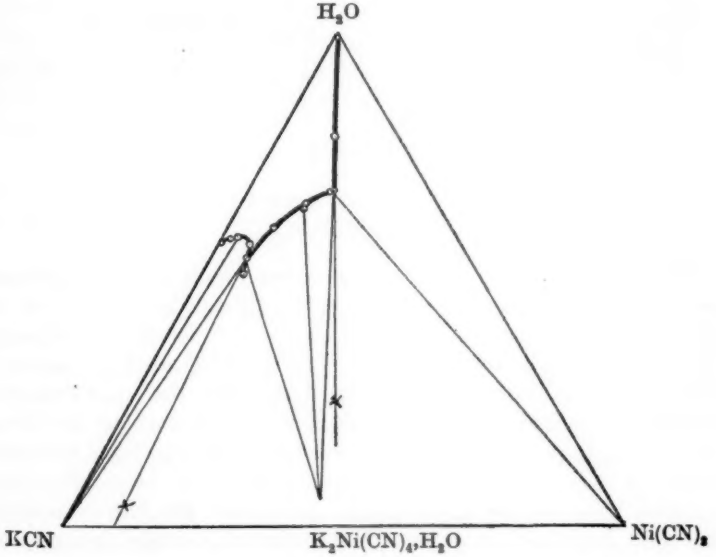
FIG. 3.



Haidlen and Fresenius (*loc. cit.*), Balard (*Compt. rend.*, 1844, **19**, 909), Gmelin (*loc. cit.*), and Clarke (*Jahresb.*, 1877, 43). Rammelsberg (*Pogg. Ann.*, 1837, **42**, 114) also prepared the sodium salt, $Na_2Ni(CN)_4,3H_2O$, and all other nickelocyanides described in the literature are of this type.

The equilibrium in the system KCN–$Ni(CN)_2$–H_2O was investigated at 25° and the results are given in Table IV and Fig. 4. The solubility curve of potassium cyanide, which can be followed into metastable regions, has a wider range of existence than in any other system in this investigation. In solutions in equilibrium with solid nickel cyanide, the simple cyanides are present in the stoicheiometrical ratio required for the double salt, a fact of interest in connexion with the cyanometric estimation of nickel (Treadwell, "Analytical Chemistry," II, 5th ed., 721). Essentially this method comprises addition of excess of potassium cyanide to a nickel

FIG. 4.



solution and estimation of the excess above that required to form the salt, $K_2Ni(CN)_4$, by titration with silver nitrate. From a study of the diagram it would be anticipated that accurate results should also be obtained by the reverse process of adding nickel solution to a standard solution of potassium cyanide. The objection to such a procedure, however, lies in the difficulty of determining the exact end-point of the titration.

That potassium nickelocyanide is hydrated is a matter of interest in connexion with the Langmuir–Lewis electronic theory of valency. According to this theory, the substance $K_2Ni(CN)_4,H_2O$ has 18 electrons in the outer shell, thus representing a condition of maximum stability, such as obtains with the anhydrous compounds, $K_2Zn(CN)_4$

and $K_2Cd(CN)_4$. A similar condition is found in the salt $K_2Hg(CN)_4$, which has an outer shell of 32 electrons.

TABLE IV.

The System KCN–$Ni(CN)_2$–H_2O *at* 25°.

Liquid phase.		"Rest."		
% KCN.	% $Ni(CN)_2$.	% KCN.	% $Ni(CN)_2$.	Comp. of solid phase.
41·7	0·0	—	—	KCN.
39·85	1·00	93·70	Trace	
38·79	1·88	93·73	Trace	
37·64	4·69	89·80	Trace	
* 41·11	6·56	91·33	0·77	
39·09	5·95	86·23	9·02	KCN + $K_2Ni(CN)_4,H_2O$.
30·94	7·46	—	—	$K_2Ni(CN)_4,H_2O$.
23·97	10·82	48·94	41·31	
23·14	10·34	47·15	39·96	
16·82	14·29	50·04	42·53	
16·82	13·94	38·15	35·92	$K_2Ni(CN)_4,H_2O$ + $Ni(CN)_2$.
10·58	9·13	—	—	$Ni(CN)_2$.
0·28	0·23	Trace	38·89	

* Metastable.

EXPERIMENTAL.

Zincicyanides.

Potassium cyanide. The best samples which could be procured commercially contained 2—3% of hydroxide. The presence of this impurity introduced a slight error in the solubility determinations when potassium cyanide was present in large amount. This difficulty was overcome by preparing the mixtures from weighed quantities of the constituents and deducting the known amount of potassium hydroxide present from the total potassium found in the liquid phase by analysis. This procedure seems justified, since James (*J. Soc. Chem. Ind.*, 1897, **16**, 120) showed that the solid deposited on evaporating a solution containing equivalent weights of potassium hydroxide and zincicyanide was practically pure $K_2Zn(CN)_4$. The figures given in the table have been thus corrected.

Zinc cyanide. The precipitate obtained by addition of a zinc salt to a solution of potassium cyanide contains a variable amount of basic cyanide. The zinc cyanide used was obtained as a microcrystalline powder by addition of excess of zinc sulphate to a warm solution of potassium zincicyanide. After standing over-night, the white precipitate of zinc cyanide was removed by filtration, washed with cold water, and dried in air.

Potassium zincicyanide. This was prepared in the manner described on p. 3191 [Found: KCN, 52·0; $Zn(CN)_2$, 47·2. $K_2Zn(CN)_4$ requires KCN, 52·5; $Zn(CN)_2$, 47·5%].

Water. All water used for the solubility determinations was boiled to remove carbon dioxide.

Solubility Determinations.—Mixtures of the double salt and potassium or zinc cyanide were made up in presence of water in wax bottles so that liquid and solid phases were present. After rotation in a thermostat at 25° for 1 or 2 days, the bottles were opened and the solid thoroughly ground. The bottles were then replaced in the thermostat for a further 4 or 5 days. On attainment of equilibrium, the liquid and solid phases were separated and analysed. This procedure was adopted in investigating the three remaining systems.

Analysis.—After decomposition of any complex present by warming with dilute hydrochloric acid, the zinc was separated as sulphide and weighed as pyrophosphate. The potassium remaining in the filtrate was estimated as sulphate. A microscopic examination of the solid phases confirmed the analyses, the double salt being obtained as crystals of indeterminate shape or, less frequently, as transparent octahedra.

Cadmicyanides.

Cadmium cyanide. Pure cadmium cyanide could not be prepared and the basic cyanide, $3Cd(CN)_2,CdO,4H_2O$, was used; by addition of a slight excess of strong cadmium nitrate solution to a concentrated solution of potassium cyanide, this substance was obtained as a white precipitate which increased in bulk on warming. After being washed with cold water and dried in air at 110°, it was analysed. The cadmium was precipitated as sulphide and weighed as sulphate. In two separate samples the cyanide was estimated (*a*) by warming with silver nitrate solution, removing the precipitated silver cyanide, igniting, and weighing the silver obtained; (*b*) by distillation with 0·1*N*-sulphuric acid, the hydrocyanic acid evolved being collected in dilute potassium hydroxide and titrated with silver nitrate. The second method can only be regarded as confirmatory, for, on distillation with dilute sulphuric acid, cyanides of the heavy metals frequently do not give a theoretical yield of hydrocyanic acid. That a theoretical yield would result in the present case seemed probable in view of the fact that cadmium cyanide is somewhat soluble in water and that potassium zincicyanide liberates 4 mols. of hydrocyanic acid under similar conditions [Found: Cd, 64·6; CN, (*a*) 22·4, (*b*) 22·4%, corresponding to $3Cd(CN)_2,CdO, 4·12\ H_2O$].

This basic cadmium cyanide was slightly soluble in water, giving a solution alkaline to methyl-orange. A distinct tendency towards formation of colloidal solutions was noted and this rendered solubility determinations of questionable value. The solid and liquid phases could not be separated by filtration, but the solution was removed

in a pipette fitted with a cotton-wool filter. The results give values between 0·36 and 1·25 g. of "cadmium cyanide" per 100 g. of solution, but the most probable figure appears to be in the neighbourhood of 0·37. Joannis gives the solubility of $Cd(CN)_2$ in water as 17 g. per litre at 15°.

Potassium cadmicyanide. This was readily obtained by dissolving cadmium hydroxide in aqueous potassium cyanide and slowly evaporating the solution. The colourless, hexagonal plates which separated were crystallised from water and air-dried [Found: KCN, 44·8; $Cd(CN)_2$, 55·5. $K_2Cd(CN)_4$ requires KCN, 44·2; $Cd(CN)_2$, 55·8%].

Analysis.—Cadmium was precipitated from the cold solution by hydrogen sulphide in presence of sulphuric acid. The precipitated sulphide was removed, dissolved in hydrochloric acid, and weighed after conversion into sulphate. The potassium remaining in the filtrate was estimated as sulphate, a correction being applied as before.

Microscopic examination of the solid phases showed that the double salt occurred as colourless crystals of indeterminate shape or as transparent, hexagonal plates.

Mercuricyanides.

Potassium cyanide. Recrystallisation of potassium cyanide from 60% alcohol gave a product in which the potassium present as cyanide agreed closely with the total potassium found. The potassium cyanide thus prepared did not develop a yellow colour in aqueous solution after several days, whereas the untreated substance did so.

Mercuric cyanide. "B.D.H. pure" mercuric cyanide was twice recrystallised from hot water, colourless, anhydrous crystals being obtained. The solubilities given by Sherrill (*loc. cit.*) and Herz and Anders (*Z. anorg. Chem.*, 1907, **52**, 164) for mercuric cyanide in water at 25°, when recalculated, are respectively 10·00 and 10·13 g. of salt per 100 g. of solution, in agreement with that now found.

Potassium mercuricyanide. This was obtained as large, transparent, colourless crystals of indeterminate shape by slow evaporation of a solution containing the simple cyanides in the theoretical proportions.

Analysis.—After slight acidification with hydrochloric acid, the mercury was separated and estimated as sulphide, and the potassium remaining in the filtrate was determined as sulphate.

Under the microscope, the large, transparent crystals of the double salt were readily distinguished from those of mercuric cyanide, which showed a distinct tendency to form needles.

Nickelocyanides.

Nickel cyanide. Addition of excess of nickel sulphate to an aqueous solution of potassium cyanide yielded the nickel cyanide as a bluish-green, gelatinous precipitate. After standing overnight, it was filtered off and washed with water until free from sulphate. The colour changed to pale blue on drying at 110°.

Potassium nickelocyanide. This was readily obtained by slow evaporation of an aqueous solution of potassium cyanide saturated with nickel cyanide, the potassium cyanide having been purified by alcohol as before.

Solubility Determinations.—All the solutions were orange-yellow. When nickel cyanide was present as a solid phase, filtration was slow. More difficulty in attaining equilibrium was experienced than hitherto. An attempt to obtain the isothermal invariant point [solid KCN + $K_2Ni(CN)_4,H_2O$], by addition of solid potassium cyanide to a saturated solution of the double salt in presence of excess of solid, gave a solution containing no excess of potassium cyanide, even if the mixture was maintained at 25° for 3 weeks. The results are in Table V.

TABLE V.

Liquid phase.		"Rest."		
% KCN.	% $Ni(CN)_2$.	% KCN.	% $Ni(CN)_2$.	Comp. of solid phase.
17·08	14·24	62·66	28·43	KCN + $K_2Ni(CN)_4,H_2O$.
16·98	13·92	51·23	40·46	

The invariant point given in Table IV was readily obtained by addition of excess of potassium nickelocyanide to a saturated solution of potassium cyanide.

Analysis.—Nickel was estimated by means of dimethylglyoxime. In a further portion of the solution, slightly acidified with acetic acid, the nickel was separated by means of hydrogen sulphide, and the potassium remaining in the filtrate determined as sulphate.

Under the microscope, the double salt obtained as the solid phase was seen to consist of large, orange-yellow crystals of indeterminate shape.

Summary.

A phase-rule investigation of the systems KCN–$M(CN)_2$–H_2O (where M = Zn, Cd, Hg, or Ni) has been carried out at 25°. The conditions of concentration underlying the formation of the double salts at this temperature have thus been determined. A gradual increase occurs in the solubility of the heavy-metal cyanides in aqueous solutions of their respective double salts on passing from

zinc to mercury. A similar increase is shown in the solubilities of the complex cyanides in water.

The cyanometric estimation of zinc and nickel is discussed in the light of the results obtained.

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CCCCXXXII.—*Optical Activity and the Polarity of Substituent Groups. Part V.* sec.-β-*Octyl Esters of some Substituted Acetic Acids and their Behaviour towards Solvents.*

By HAROLD GORDON RULE and ROBERT K. S. MITCHELL.

THE examination of a number of menthyl esters of substituted acetic acids (J., 1925, **127**, 2188) has shown that the influence of the substituents on rotatory power is in approximate agreement with their general polar character. β-Octyl alcohol, in comparison with menthol, appears to yield derivatives which are more complex in their optical properties, but thanks to the work of Pickard and Kenyon it is now a readily accessible compound and has been made the subject of a number of valuable researches by these investigators. It has been concluded (see also Hunter, J., 1924, **125**, 1389) that the β-octyl esters of aliphatic carboxylic acids exhibit complex dispersion, which may become anomalous under certain conditions of temperature and in the presence of certain solvents. During the course of an examination of β-butyl acetate and β-octyl acetate, heptoate, and stearate, it was found that the optical rotatory power of each ester was affected in a similar manner by a number of solvents. Ethylene dibromide, for example, brought about an exaltation in values, as compared with those for the homogeneous esters, whereas chloroform, benzene, pyridine, and carbon disulphide led to increasingly diminished values and in most cases to a reversal of sign. Now the only atoms of marked polar character in these esters are the oxygen atoms contained in the carboxyl residue, and it is of interest to determine what specific effect, if any, on the solvent action would result from the introduction of a polar substituent into the α-position to the carboxyl group.

The following pages contain an account of the preparation and properties of the optically active β-octyl esters of methoxy-, chloro-, bromo-, and iodo-acetic acids. Rotations were measured for the compounds in the homogeneous state at temperatures between 20° and 95°, and for the four wave-lengths λ_{4358}, λ_{5461}, λ_{5780},

and λ_{5893}. Determinations were also made of the rotatory powers of these compounds in 5% solution in a number of solvents. The molecular rotations, $[M]_D$, for the homogeneous esters at 20°, 40°, 60°, 80°, and 90° are summarised in Table I. The values of $[M]_D$ in solution at 20° are given in Table II, in which the figures found by Pickard and Kenyon for β-octyl acetate are also included for the purpose of comparison.

TABLE I.

Values of $[M]_D$ *for the* d-β-*Octyl Esters* of Monosubstituted Acetic Acids in the Homogeneous State.*

t.	Methoxy-ester.	Chloro-ester.	Bromo-ester.	Iodo-ester.
20°	+16·3°	+17·9°	+28·8°	+43·7°
40	14·8	16·4	26·5	40·9 (at 37·9°)
60	13·5	15·1	24·5	37·4 (at 62°)
80	12·4	14·0	23·0	—
90	12·0	13·5	22·4	—

* To avoid confusion, the figures in Tables I and II are all quoted as for derivatives of *d*-octyl alcohol, although in some cases the experimental work was actually carried out with the *l*-isomeride. The values are read off from the smooth curves obtained from the figures given in the experimental section.

TABLE II.

Molecular Rotations, $[M]_D^{20°}$, *of* d-β-*Octyl Esters in Various* 5% *Solutions.*

Solvent.	Acetate.	Methoxy-acetate.	Chloro-acetate.	Bromo-acetate.	Iodo-acetate.
Ethylene dibromide	+16·8°	+19·2°	+21·3°	+30·3°	+41·1°
(Homogeneous ester) ...	+11·8	+16·3	+17·9	+28·8	+43·7
s-Tetrachloroethane	+10·2	+11·4	+13·4	+21·5	+35·7
Acetone	+ 9·6	+11·9	+13·2	+25·2	+45·3
Nitromethane	+ 9·0	+12·4	+14·1	+23·8	+41·9
Ethyl acetate	+ 8·9	+12·5	+14·9	+26·5	+45·1
Chloroform	+ 6·5	+11·6	+12·6	+22·7	+38·3
Acetic acid	+ 6·3	+11·6	+11·5	+25·9	+43·0
Ethyl alcohol	+ 6·1	+11·3	+12·9	+26·4	+46·8
Carbon tetrachloride.....	+ 6·0	+13·0	+16·4	+28·0	+41·4
Toluene	—	+ 0·8	—	+10·8	—
Benzene	− 1·4	− 1·0	+ 0·8	+10·1	+18·9
Phenetole	− 2·4	− 6·4	− 5·2	+ 4·9	+16·4
Chlorobenzene	− 5·3	− 7·1	− 6·7	+ 2·5	+12·1
Bromobenzene	—	− 7·0	− 8·8	+ 1·6	+ 9·1
Pyridine	− 6·5	−11·5	(−11·6)*	(−56·6)*	(−52·4)*
Iodobenzene	—	−12·7	− 9·9	− 1·0	+ 2·9
Carbon disulphide	−15·4	−14·7	−10·7	− 1·2	+ 7·1

* These figures represent combination with solvent.

Influence of Substitution.

It will be seen from the figures in Table I that the molecular rotations are comparatively low in magnitude, although higher than

that for the unsubstituted ester. In each case the values fall rapidly as the temperature rises, a property which is also common to octyl alcohol and octyl acetate (Pickard and Kenyon, J., 1911, **99**, 45; 1914, **105**, 835).

For the purpose of determining the relative effects of different substituents, the values of $[M]_D^{20°}$ may be compared with those recorded by Pickard and Kenyon for β-octyl acetate, propionate and butyrate.

Substituent.	H.	Me.	OMe.	Et.	Cl.	Br.	I.
$[M]_D^{20°}$	+11·8°	13·0°	16·3°	17·9°	17·9°	28·8°	43·7°

Here the relative influence of the three halogen atoms is the reverse of that found for the corresponding menthyl esters (Hilditch, J., 1912, **101**, 202) and for the menthyl esters of ortho-substituted benzoic acids (Cohen, J., 1914, **105**, 1892), in which cases the effect of the halogen increases with decreasing atomic weight. A change in the above sense has, however, been recorded for the nuclear-substituted methyl dibenzoyltartrates (Frankland, Carter, and Adams, J., 1912, **101**, 2470), where the relative influence is also given by H<Me<Cl<Br<I.

Except for the reverse order of the halogens among themselves, the effect of substituents on the rotatory power of β-octyl acetate, *viz.*, H<Me<OMe<Et<Cl<Br<I, is in approximate agreement with their general polar character, H<(Me,Et)<OMe<I<Br<Cl, as deduced from their influence on the molecular inductive capacity of benzene or an aliphatic hydrocarbon (J., 1924, **125**, 2159). A somewhat similar group arrangement holds for the rotatory powers of the corresponding menthyl esters of substituted acetic acids, where H<(Et,Me)<OMe<I<Br<Cl (J., 1925, **127**, 2189); for the dissociation constants of substituted acetic acids, (Et,Me)< H<OMe<I<Br<Cl; and for a number of cases of chemical reactivity (J., 1924, **125**, 2159).

In this connexion, it does not appear to have been previously pointed out that the initial disturbances observed by Pickard and Kenyon in the rotatory powers of certain homologous series of aliphatic esters, which may take the form of a depression at the C_3 acid followed by an exaltation at the C_5 acid, are paralleled by a similar disturbance in the dissociation constants of the acids. It is, in fact, becoming increasingly evident that the alteration in rotatory power due to a change in the molecular structure of an active compound often goes hand in hand with the effect of this change on other properties such as acidity, inductive capacity and chemical reactivity. An example of the last type has already been observed in the relationship existing between the influence of

substituents on further substitution in the benzene nucleus and on the rotatory power of the menthyl and β-octyl esters of *o*-substituted benzoic acids (Rule, J., 1924, **125**, 1121; Rule and Numbers, this vol., p. 2166). In many cases, however, these resemblances are masked by other effects, such as those due to dispersion. Another group effect of a hitherto undiscovered type is described later under "influence of solvents."

Dispersion.

When the values of $1/\alpha$ for the above substituted acetic esters are plotted against λ^2, it is found that the points do not lie on straight lines, the divergence being greater at the higher temperatures of experiment than at the lower. The substituted esters therefore resemble the parent compound in showing complex dispersion. This is specially marked for the esters in carbon disulphide solution, and when the rotations are plotted in the form of a characteristic diagram the points representing the values in this solvent fall outside the lines accommodating the remaining points. A small region of anomalous dispersion exists where the molecular rotations of the *d*-octyl esters approximate to $+3°$.

Influence of Solvents.

The figures in Table II reveal a number of interesting regularities in the variation of rotatory power with change of solvent and in the effect of substituents contained in the solvent molecule.

Variation of Rotatory Power with Change of Solvent.—The first point to be observed is that the rotatory powers of all five esters are affected in a very similar manner by solvent action. In every case, a maximum depression is produced in carbon disulphide solution, which in general reverses the sign of rotation, and with the exception of the iodo-compound each ester gives an increased value in ethylene dibromide. All the aromatic solvents, including pyridine, resemble carbon disulphide in diminishing the rotatory powers. Owing to the low values of the observed rotations, it is possible that a few of the minor displacements in the columns are due to experimental errors, but the differences displayed by the iodo-ester are more definite, and are chiefly connected with the relatively higher values given by the oxygen-containing solvents ethyl alcohol, acetone, ethyl acetate, and acetic acid. It is significant that the substituent having the most pronounced effect on the rotatory power of the parent ester should also bring about the most specific changes in the behaviour of the substituted esters towards solvents. Pyridine, as might be expected, combines readily with the halogen derivatives. When it is mixed with the bromo-

or iodo-ester, heat is developed and the rotation rises rapidly to a limiting value.

A second point of interest is that the order of the rotatory powers of the five esters in any given solvent is the same as that for the esters in the homogeneous state. The only exceptions to this statement are small displacements of the values for the acetate in pyridine, chlorobenzene, and phenetole, and for the chloro-ester in bromobenzene.

These regularities appear to show that solvents influence the rotatory power chiefly through the medium of the carboxyl group, and that any specific solvent effect due to the presence of the substituents in question is a minor one. This is in agreement with the comparatively weak polar character of the substituents and their greater distance from the asymmetric complex.

Effect of Substituents in the Solvent Molecule.—On comparing the changes produced in the rotatory powers of the esters by solution in benzene or one of its substituted derivatives, it will be seen that toluene produces the least and iodobenzene the greatest alteration in value. The relative depressions due to the entry of different substituents into the benzene molecule are given by Me<H<OEt<Cl<Br<I, and this sequence holds for all five esters. In view of the fact that no connexion has yet been established between the nature of a solvent and its influence on the optical rotation of a dissolved substance, it is a point of unusual interest that this series so closely resembles that representing the effect of the substituents when introduced into the molecule of β-octyl acetate, *viz.*, H<Me<OMe<Cl<Br<I. In both cases, the order of the halogens among themselves is the reverse of that which might have been expected from their relative polarity, but whereas substitution in the asymmetric molecule increases the positive rotation of the *d*-ester, substitution in the solvent benzene molecule diminishes the positive rotation. It is probable that efforts to determine the relationship between rotatory power and solvent influence would be attended by a greater measure of success if more use were made of solvent series such as the above, in which the character of the molecule as a whole does not undergo any violent change from member to member.

Experimental.

The general method of procedure employed in the preparation and examination of the esters has been described in earlier communications (J., 1925, **127**, 2188; this vol., p. 2116). The first three compounds mentioned below were prepared from the corresponding acid chlorides, the iodo-ester being obtained from the chloro-ester by treatment with ethereal magnesium iodide (Bodroux and Taboury,

Bull. Soc. chim., 1907, **1**, 909). All the esters are colourless, odourless liquids.

β-*Octyl methoxyacetate*, b. p. 120°/15 mm. (Found: C, 65·2; H, 11·1. $C_{11}H_{22}O_3$ requires C, 65·3; H, 11·0%).

β-*Octyl chloroacetate*, b. p. 119—120°/15 mm. (Found: Cl, 17·6. $C_{10}H_{19}O_2Cl$ requires Cl, 17·2%).

β-*Octyl bromoacetate*, b. p. 121°/15 mm. (Found: Br, 31·7. $C_{10}H_{19}O_2Br$ requires Br, 31·8%).

β-*Octyl iodoacetate*, b. p. 146—147°/17 mm. (Found: I, 42·6. $C_{10}H_{19}O_2I$ requires I, 42·6%).

Densities and Rotatory Powers of the Esters in the Homogeneous State.

Rotations were determined in a 1-dcm. tube, except those for the methoxy-ester and others marked with an asterisk, which were measured in a 0·5-dcm. tube.

Observed Densities and Rotations.

Octyl methoxyacetate.

$D_4^{t°}$	0·9721 at 20·5°; 0·9568 at 40·7°; 0·9435 at 57·6°; 0·9253 at 80·9°.
α_{5893}	3·90° at 20·9°; 3·51° at 38·5°; 3·20° at 60·5°; 2·70° at 93·7°.
α_{5780}	4·08° at 20·5°; 3·65° at 38·7°; 3·33° at 60·4°; 2·81° at 93·2°.
α_{5461}	4·60° at 20·7°; 4·12° at 38·6°; 3·73° at 60·9°; 3·20° at 93·7°.
α_{4358}	7·33° at 20·6°; 6·52° at 38·5°; 5·88° at 60·3°; 4·84° at 93·5°.

Octyl chloroacetate.

$D_4^{t°}$	0·9900 at 20·3°; 0·9747 at 39·4°; 0·9603 at 58·4°; 0·9413 at 81·1°.
α_{5893}	8·64° at 18·7°; 7·82° at 38·2°; 7·06° at 59·5°; 6·13° at 89·9°.
α_{5780}	9·04° at 19·0°; 8·24° at 38·3°; 7·21° at 59·6°; 6·47° at 90·0°.
α_{5461}	10·14° at 18·6°; 9·19° at 38·3°; 8·10° at 59·7°; 7·24° at 89·7°.
α_{4358}	16·09° at 18·8°; 14·78° at 38·7°; 12·94° at 59·7°; 11·51° at 90·3°.

Octyl bromoacetate.

$D_4^{t°}$	1·1731 at 22·6°; 1·1549 at 40·8°; 1·1360 at 59·6°; 1·1127 at 83·8°.
α_{5893}	13·34° at 22·0°; 12·40° at 37·8°; *5·67° at 53·4°; *5·20° at 75·6°.
α_{5780}	13·89° at 22·5°; 13·02° at 37·5°; *6·03° at 53·4°; *5·49° at 75·4°.
α_{5461}	15·71° at 22·5°; 14·67° at 37·7°; *6·75° at 53·4°; *6·24° at 75·7°.
α_{4358}	26·58° at 22·0°; 24·72° at 37·7°; *11·29° at 53·5°; *10·24° at 75·4°.

Octyl iodoacetate.

$D_4^{t°}$	1·3013 at 21·2°; 1·2812 at 41·9°; 1·2587 at 64·3°.
α_{5893}	19·08° at 20·0°; 17·63° at 37·9°; 15·79° at 62°.
α_{5780}	19·89° at 20·0°; 18·32° at 37·9°; 16·36° at 63°.
α_{5461}	22·72° at 19·8°; 20·89° at 37·8°; 18·58° at 63°.
α_{4358}	39·49° at 19·7°; 36·10° at 38·2°; 31·80° at 63°.

Rotatory Powers of the Esters in Solution (approx. 5%) at 20°.

The solvents employed were the purest products obtainable and were in all cases submitted to further purification. The acetone

used was "from the bisulphite compound." Alcohol was dehydrated over calcium. Owing to the yellow colour of the iodobenzene it was not possible to obtain measurements of α_{4358} in this solvent. The values for the halogen esters in pyridine represent compound formation, the rotations for the bromo- and iodo-esters rising continuously from the time of the first observation.

Rotatory Power of l-β-*Octyl Methoxyacetate in Solvents.*

$l = 2$, except for solvents marked, where $l = 1$. w = weight in g. of ester in 25 c.c., or * in 10 c.c.

Solvent.	w.	α_{5893}.	α_{5461}.	α_{4358}.	$[M]_{5461}$.	$[M]_{4358}$.
$C_2H_4Br_2$	1·2242	−0·93°	−1·06°	− 1·80°	−21·9°	−37·0°
Ester (homog.)	—	−7·86	−9·26	−14·70	−19·25	−30·56
CCl_4	1·2267	−0·63	−0·72	− 1·15	−14·8	−23·7
$CH_3{\cdot}CO_2Et$	1·1931	−0·59	−0·71	− 1·15	−15·0	−24·4
$CH_3{\cdot}NO_2$	1·2055	−0·59	−0·70	− 1·12	−14·7	−23·5
$(CH_3)_2CO$	1·2503	−0·59	−0·67	− 1·11	−13·5	−22·4
$CH_3{\cdot}CO_2H$	1·1961	−0·55	−0·63	− 0·97	−13·3	−20·5
$CHCl_3$	1·2015	−0·55	−0·62	− 0·97	−13·0	−20·4
s-$C_2H_2Cl_4$	1·2872	−0·58	−0·64	− 1·04	−12·6	−20·4
C_2H_6O	1·2285	−0·55	−0·64	− 1·04	−13·2	−21·4
C_7H_8	1·3013	−0·04	—	—	—	—
C_6H_6	1·2710	+0·05	+0·07	+ 0·24	+ 1·4	+ 4·8
$C_6H_5{\cdot}OEt$	1·1883	+0·30	+0·34	+ 0·72	+ 7·2	+15·3
C_6H_5Cl	0·5141*	+0·18	+0·23	+ 0·44	+ 9·0	+17·3
C_6H_5Br	0·5198*	+0·18	+0·23	+ 0·44	+ 8·9	+17·1
C_5H_5N	1·2290	+0·56	+0·68	+ 1·16	+14·0	+23·9
C_6H_5I	0·4945*	+0·31	+0·37	—	+15·1	—
CS_2	1·2058	+0·70	+0·79	+ 1·80	+16·6	+37·7

Rotatory Power of l-β-*Octyl Chloroacetate in Solvents.*

$l = 2$, except for solvents marked, where $l = 1$. w = weight in g. of ester in 25 c.c., or * in 10 c.c.

Solvent.	w.	α_{5893}.	α_{5461}.	α_{4358}.	$[M]_{5461}$.	$[M]_{4358}$.
$C_2H_4Br_2$	1·2710	−1·05°	− 1·20°	− 2·06°	−24·4°	−41·9°
Ester (homog.)	—	−8·58	−10·06	−16·03	−20·99	−33·45
CCl_4	1·2133	−0·77	− 0·91	− 1·48	−19·4	−31·5
$CH_3{\cdot}CO_2Et$ ...	1·2322	−0·71	− 0·90	− 1·43	−18·9	−30·0
$CH_3{\cdot}NO_2$	1·2635	−0·69	− 0·80	− 1·25	−16·3	−25·6
s-$C_2H_2Cl_4$	1·2284	−0·64	− 0·74	− 1·27	−15·6	−26·7
$(CH_3)_2CO$	1·2688	−0·65	− 0·80	− 1·23	−16·3	−25·0
C_2H_6O	1·2806	−0·64	− 0·78	− 1·21	−15·7	−24·4
$CHCl_3$	1·2252	−0·60	− 0·72	− 1·10	−15·2	−23·2
$CH_3{\cdot}CO_2H$	1·2078	−0·54	− 0·66	− 1·06	−14·1	−22·7
C_6H_6	1·2592	−0·04	− 0·05	− 0·09	− 1·0	− 1·8
$C_6H_5{\cdot}OEt$	1·1941	+0·24	+ 0·32	+ 0·60	+ 6·9	+13·0
C_6H_5Cl	0·4950*	+0·16	+ 0·23	+ 0·41	+ 9·6	+17·1
C_6H_5Br	0·4924*	+0·21	+ 0·22	+ 0·42	+ 9·2	+17·6
C_6H_5I	0·4988*	+0·24	+ 0·29	—	+12·0	—
CS_2	1·2677	+0·51	+ 0·66	+ 1·52	+13·9	+32·0
C_5H_5N	1·2677	(+0·57)	—	—	—	—

Rotatory Power of l-β-*Octyl Bromoacetate in Solvents.*

$l = 2$, except for solvents marked, where $l = 1$. w = weight in g. of ester in 25 c.c., or * in 10 c.c.

Solvent.	w.	a_{5893}.	a_{5461}.	a_{4358}.	$[M]_{5461}$.	$[M]_{4358}$.
$C_2H_4Br_2$	1·2109	− 1·17°	− 1·32°	− 2·32°	−34·2°	−60·1°
Ester (homog.)	—	−13·46	−15·97	−26·85	−34·10	−57·37
CCl_4	1·2654	− 1·13	− 1·37	− 2·33	−34·0	−57·8
$CH_3{\cdot}CO_2Et$ ...	1·2657	− 1·07	− 1·29	− 2·20	−32·0	−54·6
C_2H_6O	1·2584	− 1·06	− 1·28	− 2·17	−31·9	−54·1
$CH_3{\cdot}CO_2H$	1·2618	− 1·04	− 1·22	− 2·10	−30·3	−52·2
$(CH_3)_2CO$	1·1302	− 0·91	− 1·12	− 1·82	−31·1	−50·5
$CH_3{\cdot}NO_2$	1·2537	− 0·95	− 1·16	− 1·99	−29·0	−49·8
$CHCl_3$	1·2159	− 0·88	− 1·02	− 1·69	−26·3	−43·6
s-$C_2H_2Cl_4$	1·3139	− 0·90	− 1·07	− 1·76	−25·6	−42·0
C_7H_8	0·5238*	− 0·22	—	—	—	—
C_6H_6	1·2478	− 0·40	− 0·46	− 0·78	−11·6	−19·6
$C_6H_5{\cdot}OEt$	1·3415	− 0·21	− 0·28	− 0·39	− 6·5	− 9·1
C_6H_5Cl	0·4970*	− 0·05	− 0·06	− 0·09	− 3·0	− 4·5
C_6H_5Br	0·4607*	− 0·03	− 0·04	− 0·06	− 2·2	− 3·3
C_6H_5I	0·5130*	+ 0·02	+ 0·05	—	+ 2·4	—
CS_2	1·2924	+ 0·05	+ 0·07	+ 0·39	+ 1·7	+ 9·5
C_5H_5N	1·2641	(+ 2·28)	—	—	—	—

Rotatory Power of d-β-*Octyl Iodoacetate in Solvents.*

$l = 2$, except for solvents marked, where $l = 1$. w = weight in g. of ester in 20 c.c., or * in 10 c.c., or † in 25 c.c.

Solvent.	w.	a_{5893}.	a_{5461}.	a_{4358}.	$[M]_{5461}$.	$[M]_{4358}$.
C_2H_6O	1·0310	+ 1·62°	+ 1·97°	+ 3·36°	+57·0°	+97·1°
$(CH_3)_2CO$	1·0066	+ 1·53	+ 1·82	+ 3·17	+53·9	+93·8
$CH_3{\cdot}CO_2Et$ ...	1·0184	+ 1·54	+ 1·84	+ 3·21	+53·9	+94·9
Ester (homog.)	—	+19·08	+22·72	+39·49	+51·98	+90·33
$CH_3{\cdot}CO_2H$	0·4846*	+ 0·70	+ 0·84	+ 1·48	+51·6	+91·0
$CH_3{\cdot}NO_2$	0·5050*	+ 0·71	+ 0·87	+ 1·53	+51·4	+90·3
CCl_4	1·0232	+ 1·42	+ 1·70	+ 3·00	+49·5	+87·4
$C_2H_4Br_2$	0·9941	+ 1·37	+ 1·64	+ 2·79	+49·2	+83·7
$CHCl_3$	1·0279	+ 1·32	+ 1·55	+ 2·64	+45·0	+76·5
s-$C_2H_2Cl_4$.....	0·5425*	+ 0·65	+ 0·76	+ 1·35	+41·8	+74·2
C_6H_6	1·2837†	+ 0·65	+ 0·78	+ 1·35	+22·7	+39·2
$C_6H_5{\cdot}OEt$	0·9964	+ 0·55	+ 0·65	+ 1·10	+19·4	+32·9
C_6H_5Cl	0·4917*	+ 0·20	+ 0·23	+ 0·44	+13·9	+26·7
C_6H_5Br	0·4896*	+ 0·15	+ 0·17	—	+10·3	—
CS_2	0·9690	+ 0·23	+ 0·26	+ 0·26	+ 8·0	+ 8·0
C_6H_5I	0·5168*	+ 0·05	+ 0·07	—	+ 4·0	—
C_5H_5N	1·1197	(− 1·97)	—	—	—	—

In conclusion the authors desire to thank the Earl of Moray Fund for a grant which has covered most of the expenses incurred in this investigation.

UNIVERSITY OF EDINBURGH. [*Received, October 20th,* 1926.]

CCCCXXXIII.—*The Crystalline Forms of 5-Nitrosalicylic Acid and of Related Compounds.*

By FREDERICK DANIEL CHATTAWAY and WILLIAM RYLE CLIFFORD CURJEL.

WHEN a hot saturated aqueous solution of 5-nitrosalicylic acid is cooled to the ordinary temperature, the acid separates as slender, hair-like, almost colourless needles, the whole liquid becoming a felted pulp. On separating these crystals, suspending them in a small quantity of the mother-liquor, and warming, compact crystals appear, and grow at the expense of the slender needles, which quickly dissolve and disappear. On allowing the compact crystals to remain in contact with the aqueous mother-liquor at the ordinary temperature, the hair-like form reappears and grows slowly at the expense of the compact crystals, which in their turn dissolve and finally disappear.

When the hair-like crystals are separated from the aqueous mother-liquor and placed in a little alcohol or acetone at the ordinary temperature, compact crystals, identical with those obtained by heating in aqueous suspension, make their appearance and grow at the expense of the needle-shaped form, which, as before, dissolves and finally disappears.

These phenomena are due to the formation and decomposition of a hitherto unrecognised monohydrated form of the acid, which crystallises in hair-like needles, the compact form being the anhydrous acid.

The hydrated form readily loses water on exposure to the air, and, on account of the fine hair-like character of the crystals, great difficulty is experienced in drying them for analysis. This could only be done by exposing them for a long period to a current of air saturated with water-vapour at the equilibrium pressure of the system hydrate–anhydrous acid–vapour (compare Hill and Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 546).

The solubility of the acid in water over the temperature range 15—100° has been determined. The intersection of the respective solubility curves for the anhydrous acid and the monohydrate shows that the transition point lies in the immediate neighbourhood of 42·5°.

In the course of this work, crystals of the compact anhydrous form of 5-nitrosalicylic acid have been examined. Crystals of this acid have previously been examined by Fels (*Z. Kryst. Min.*, 1903, **37**, 486), who obtained them from solution in acetone. The crystals were described as monoclinic with axial elements $a : b : c =$

0·9692 : 1 : 1·1067; $\beta = 92° 5'$. No crystals corresponding to this description have been observed during the present examination.

Crystals of ethyl 5-nitrosalicylate have also been examined.

Experimental.

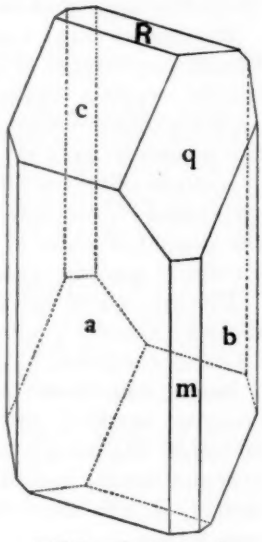
The 5-nitrosalicylic acid used was prepared by the direct nitration of salicyclic acid in acetic acid solution (compare Raiziss and Proskouriakoff, *J. Amer. Chem. Soc.*, 1922, **44**, 791), and was purified by repeated crystallisation from water.

Anhydrous 5-Nitrosalicylic Acid.—On account of the great solubility of the acid in all common organic solvents, it was difficult to obtain crystals suitable for measurement. Those used in this work were obtained by allowing solutions in acetic acid or in a mixture of acetone and ethyl acetate to cool during 3 days in a slow cooler.

The crystals belong to the holohedral class of the anorthic system. The axial elements are $a : b : c = 1·7456 : 1 : 1·0945$; $\alpha = 96° 16'$, $\beta = 114° 6'$, $\gamma = 88° 40'$.

The forms observed were $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $M\{\bar{1}10\}$, $R\{\bar{1}01\}$, and $q\{011\}$.

The interfacial angles (based on the three best crystals measured) are shown in the accompanying table.



5-Nitrosalicylic acid.

Angle.	No.	Limits.	Mean observed.	Calc.
100 : 110	6	56° 39′—57° 25′	57° 5′	*
110 : 010	6	31° 4′—31° 58′	31° 33′	*
100 : 001	6	65° 32′—66° 16′	65° 52′	*
001 : 010	6	83° 18′—84° 15′	83° 43′	*
001 : 011	4	41° 36′—42° 6′	41° 51′	*
$\bar{1}00 : \bar{1}10$	6	59° 1′—59° 32′	59° 18′	59° 3′
$\bar{1}10 : 010$	6	31° 19′—32° 20′	31° 53′	32° 19′
$001 : \bar{1}01$	6	37° 5′—37° 52′	37° 25′	37° 22′
$110 : 011$	2	38° 29′—38° 39′	38° 34′	39° 0′
$\bar{1}01 : 011$	2	53° 17′—53° 33′	53° 25′	53° 0′

There is a perfect cleavage parallel to $q\{011\}$. The resultant cleavage fragments show a biaxial interference figure, apparently symmetrical to the centre of the field. Strong crossed dispersion is shown. The double refraction is strong and negative. The axial angle is fairly wide. $\rho < v$.

Twin-crystals are frequently found, twinned on the plane $\{011\}$.

The density of the crystals is 1·654 at 18·5°.

Monohydrated 5-Nitrosalicylic Acid, $OH{\cdot}C_6H_3(NO_2){\cdot}C(OH)_3$.—To obtain crystals of the hydrate as large as possible, an aqueous solution of 5-nitrosalicylic acid, saturated below the transition point at 40°, was allowed to cool to the ordinary temperature during 2 days in a slow cooler. The hydrated form separated in very slender, strongly doubly-refractive, elongated prisms. A biaxial interference figure of narrow axial angle is visible through one of the prism faces. The figure appears to be symmetrical, and is markedly different from that shown by the anhydrous acid.

The symmetrical appearance of this figure, together with the frequent occurrence of straight extinction on the prism faces of the smaller crystals, indicates that the crystals of the hydrate are probably orthorhombic, but it has not been found possible to confirm this definitely, since no measurable crystals could be obtained.

Analysis of the hydrate. The anhydrous acid did not lose weight on prolonged heating in an air-bath at 100—120°, and, consequently, the amount of water in the hydrate could be determined by heating a weighed quantity at this temperature.

The crystals of the hydrate were freed from adhering water in the way already mentioned and were apparently dry after about 7 hours' treatment. The passage of air was continued for a further 2 hours, and about half the hydrate was then transferred to a crucible, weighed, and dehydrated by heating in an air-bath at 100—120° to constant weight (Found : loss, 9·3%). The passage of air over the second half of the hydrate was continued for a further 6 hours; it was then similarly weighed and dehydrated (Found : loss, 9·1%).

In another experiment, a further quantity of hydrate was similarly dried for 2 days [Found : loss, 9·0%. $OH{\cdot}C_6H_3(NO_2){\cdot}C(OH)_3$ requires loss, 8·95%].

Determination of the Transition Point between the Monohydrate and the Anhydrous Acid.—(a) *Dilatometric experiments.* A dilatometer was filled with an intimate mixture of the anhydrous acid and the monohydrate in presence of water, and the direction of any volume change occurring in the system noted at various constant temperatures. At all temperatures between 15° and 37°, a very slight progressive decrease of volume, and at temperatures above 46° a very slight progressive increase of volume, was observed. The transition point accordingly lay between these limits. The volume changes were, however, very slow and slight, and at temperatures between these limits were so slow as not to be perceptible.

(b) *Solubility measurements.* A number of experiments showed that aqueous and aqueous-alcoholic solutions of 5-nitrosalicylic acid could be evaporated to dryness at 100—120° without any loss of

acid, the amount of which in such solutions could be determined by weighing the residue. Its slight solubility in water, however, necessitated the evaporation of inconveniently large volumes and it was found that the quantity dissolved could be ascertained with equal accuracy by titrating sufficiently diluted solutions with standard $N/100$-alkali, the end-point being shown by the appearance of a permanent distinctive yellow colour. The most consistent results are obtained with solutions containing not more than 0·15 g. of acid in 100 c.c. In stronger solutions, the faint yellow colour of the acid itself obscures the end-point.

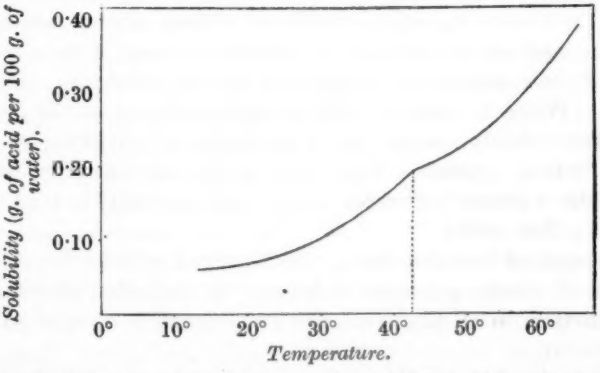
By either method small quantities of 5-nitrosalicylic acid can be estimated with a maximum error of 1%.

The saturated solutions, prepared by shaking tightly corked bottles containing water and excess of the hydrated acid for 3—4 hours in a thermostat, were aspirated into a weighing pipette through a plug of cotton wool. The amounts withdrawn, after weighing, were transferred to a calibrated flask and diluted to the uniform strength required for titration.

The results are given below; the solubility, s, is expressed as g. of acid per 100 g. of water. It was not found possible to determine metastable solubilities, since partial transformation always occurred.

Hydrated acid.				Anhydrous acid.			
Temp.	s.	Temp.	s.	Temp.	s.	Temp.	s.
14·95°	0·061	31·0°	0·103	45·0°	0·200	65·0°	0·391
17·5	0·064	33·0	0·115	50·1	0·228	72·0	0·501
20·5	0·068	35·0	0·125	55·2	0·273	74·1	0·528
25·0	0·078	36·6	0·139	60·0	0·325	99·5	1·505
29·0	0·093	40·1	0·169				

The change from the hydrated to the anhydrous form did not occur at 41°, but occurred at 43·5°. Hence the transition point lies



between these limits. By plotting the solubility–temperature curve for each solid phase and prolonging the curves to their intersection,

it is seen that the transition point lies in the immediate neighbourhood of 42·5°.

Crystallographic Examination of Ethyl 5-Nitrosalicylate.—The ester was prepared by heating 5-nitrosalicylic acid with excess of ethyl alcohol in presence of a little concentrated sulphuric acid. The liquid was poured on to ice; the ester which separated crystallised from alcohol, in which it was readily soluble, in colourless, prismatic crystals, m. p. 96°.

Crystals were obtained for measurement by allowing a solution in carbon tetrachloride to cool during 3 days in a slow cooler. The crystals belong to the monoclinic system and are of prismatic habit. The axial elements are $a : b : c = 0{\cdot}9530 : 1 : 0{\cdot}4377$; $\beta = 122° 38'$. The forms observed were $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $n\{120\}$, and, less frequently, $q\{011\}$.

The interfacial angles are given in the accompanying table.

Angle.	No.	Limits.	Mean observed.	Calc.
100 : 120	6	57° 57′—58° 16′	58° 5′	*
100 : 001	6	57° 2′—57° 37′	57° 22′	*
001 : 011	2	20° 8′—20° 20′	20° 14′	*
100 : 110	6	38° 33′—39° 28′	39° 0′	38° 45′
120 : 001	6	73° 16′—73° 41′	73° 24′	73° 26′

Perfect cleavage is developed parallel to $n\{120\}$. Less perfect cleavage is developed parallel to $c\{001\}$. A cleavage fragment parallel to (120) shows one optic axis, the b-axis being the acute bisectrix of the axial angle. The double refraction is very strong and positive. $\rho < v$.

The density of the crystals is 1·429 at 19°.

The Polymorphic Forms of 5-Nitro-2-ethoxybenzaldehydesemicarbazone.—The semicarbazone of 5-nitro-2-ethoxybenzaldehyde (see this vol., p. 2721) exists in two monotropic polymorphic modifications. It is very sparingly soluble in boiling alcohol, acetic acid, or acetone, and on rapidly cooling a solution in any of these solvents a labile form separates in clusters of almost colourless, prismatic crystals. These, in contact with the mother-liquor at the ordinary temperature, slowly change into a stable form consisting of small, brilliant yellow crystals. This form is also obtained on allowing an alcoholic solution, saturated at the boiling point, to cool during 3 days in a slow cooler.

The crystals of the labile form, which are not suitable for measurement, are of slender prismatic habit and strongly doubly-refractive. The extinction on all the prism faces examined is oblique with the interfacial edges.

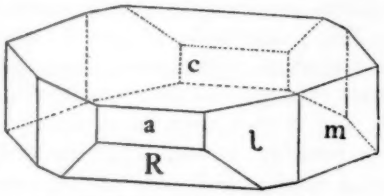
The crystals of the stable form belong to the monoclinic system. The axial elements are $a : b : c = 1{\cdot}3963 : 1 : 2{\cdot}1269$; $\beta = 104° 26'$.

The forms observed were $a\{100\}$, $l\{210\}$, $m\{110\}$, $c\{001\}$, and, less frequently, $R\{\bar{1}01\}$.

The interfacial angles are given in the accompanying table.

Angle.	No.	Limits.	Mean observed.	Calc.
100 : 001	4	75° 0′—75° 49′	75° 34′	*
100 : 210	12	33° 50′—34° 20′	34° 4′	*
001 : $\bar{1}01$	4	66° 57′—67° 38′	67° 11′	*
110 : 210	12	19° 10′—19° 37′	19° 22′	19° 27′
001 : 210	4	78° 19′—78° 32′	78° 26′	78° 5′

Fair cleavage occurs parallel to $c\{001\}$. The density of the crystals of the stable form at 18·5° is 1·437.



Semicarbazone of 5-nitro-2-ethoxybenzaldehyde.

At 20°, 100 g. of alcohol, of chloroform, and of acetone dissolve 0·10 g., 0·05 g., and 0·30 g., respectively, of the stable form.

The very slight solubility of the semicarbazone in all solvents, together with the fact that, on shaking in the thermostat, the transformation into the stable form is rapid, has prevented the solubility of the labile form from being determined.

THE QUEEN'S COLLEGE, OXFORD. [*Received, October 25th*, 1926.]

CCCCXXXIV.—*The Mercuration of Aromatic Substances. Part III.* p- *and* m-*Nitrotoluenes.*

By SAMUEL COFFEY.

RECENT quantitative investigations on the mercuration of relatively simple benzenoid compounds, *e.g.*, nitrobenzene (Dimroth, *Annalen*, 1926, **446**, 148; Jürgens, *Rec. trav. chim.*, 1926, **45**, 61), toluene (Coffey, J., 1925, **127**, 1029), and *o*-nitrotoluene (Coffey, this vol., p. 637; Burton, Hammond, and Kenner, *ibid.*, p. 1802), have clearly proved that these reactions do not follow the usual laws of substitution (compare also Coffey, *Chem. Weekblad*, 1926, **23**, 194). The study of this type of substitution has now been extended to *p*- and *m*-nitrotoluenes. A third substituent enters the former compound as a rule exclusively in position 2, but the mercuration is "abnormal" in that a large quantity of the compound substituted in the 3-position is formed; in fact, this may constitute as much as 80% of the mono-substitution products isolated. Therefore, as with toluene and *o*-nitrotoluene, the mercuration of *p*-nitrotoluene appears

to depend mainly on the nature of the entering group. Owing to the antagonistic orienting powers of the methyl and the nitro-group in *m*-nitrotoluene, substituents may enter the nucleus in positions 2, 4, 5, and 6 (compare Holleman, "Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910, pp. 310—314), and it is impossible to decide what the normal course of the reaction should be.

Reissert (*Ber.*, 1907, **40**, 4209) has obtained derivatives of *p*-nitrotoluene mercurated in the side chain, but no compounds have yet been described containing mercury directly attached to the aromatic nucleus. Such compounds are readily produced, however, by heating *p*-nitrotoluene with mercuric acetate at 140°.

The proportions of the 2- and 3-*acetoxymercuri*-4-*nitrotoluenes* obtained on mercuration were determined by converting the product through the chloromercuri-*p*-nitrotoluenes into a mixture of 2- and 3-bromonitrotoluenes and analysing this thermally. For comparison, 2- and 3-bromonitrotoluenes were prepared and the final melting points of the binary mixture determined. The two substances behaved normally, no compounds or solid solutions being formed.

Pure individual products could not be isolated from the mercuration mixture and therefore the two components were made synthetically.

2-*Chloromercuri*-4-*nitrotoluene* was prepared from the corresponding sulphinic acid (compare Peters, *Ber.*, 1905, **38**, 2567), obtained by warming the sulphonyl chloride with sodium sulphite (compare Blomstrand, *Ber.*, 1870, **3**, 965; Limpricht, *ibid.*, 1892, **25**, 75, 3477).

Derivatives of *p*-nitrotoluene containing a substituent in the 3-position are difficult to prepare.

3-*Chloromercuri*-4-*nitrotoluene* was synthesised by the following series of reactions: 4-Nitro-*o*-toluidine was sulphonated with chlorosulphonic acid, giving exclusively 4-*nitro*-*o*-*toluidine*-5-*sulphonic acid* (the constitution of which was proved by reducing it to 2 : 4-tolylenediamine-5-sulphonic acid; Foth, *Annalen*, 1885, **230**, 300). The diazonium derivative of this sulphonic acid was extremely stable and the elimination of the diazonium group was effected only by means of copper powder and formic acid. The 4-*nitrotoluene*-3-*sulphonic acid* thus obtained was converted into the corresponding *sulphinic acid*, and this into 3-chloromercuri-4-nitrotoluene.

3-Bromo-4-nitrotoluene was prepared from 4-nitroaceto-*m*-toluidide, which is produced to the extent of 10—15% by the usual method of nitrating aceto-*m*-toluidide (Cohen and Dakin, J., 1903,

83, 333; Cook and Brady, J., 1920, **117**, 1952). This method is slow and laborious on account of the great solubility and tendency to form supersaturated solutions of the nitroacetotoluidide. By using Menke's method (*Rec. trav. chim.*, 1925, **44**, 144) of nitration with copper nitrate and acetic anhydride, the yield of 4-nitroacetotoluidide has been increased from 10% to 50%, thus allowing of its isolation in quantity.

m-Nitrotoluene is more difficult to mercurate than the ortho-compound, but on heating with mercuric acetate for 12 hours it gave a mixture of acetoxymercuri-*m*-nitrotoluenes, which were converted into the corresponding chloromercuri-derivatives. 4- and 5-Chloromercuri-3-nitrotoluenes were isolated from this mixture and the occurrence of 6-chloromercuri-3-nitrotoluene was proved by the isolation of 6-bromo-*m*-toluidine from the mixture of amino-compounds obtained by reducing the corresponding mixture of bromonitrotoluenes.

EXPERIMENTAL.

Mercuration of p-*Nitrotoluene.*—*p*-Nitrotoluene (crystallised from petroleum) and mercuric acetate in various proportions were heated together at 140° for different lengths of time. In most cases, the product, if allowed to cool, solidified at about 100°. The hot mixture was therefore poured directly into ether (10 times the weight of nitrotoluene taken) and left over-night. The large precipitate (B) obtained consisted of unchanged mercuric acetate, mercurous acetate, and highly mercurated nitro-compounds, the proportions of which varied with the duration of heating.

The ether was distilled from the filtrate, excess of sodium chloride added, and the excess of *p*-nitrotoluene distilled in steam, the last traces being removed by boiling with water. The residue of crude monomercurichlorides (A) was dried and extracted with hot acetone, the solution boiled with animal charcoal, and the solvent removed.

The details of the experiments are:

Expt.	Nitrotoluene.	Mercuric acetate.	Time of heating.	B.	A.
I	150 g.	40 g.	4 hours	14 g.	—
II	450 „	120 „	4 „	70 „	35 g.
III	200 „	60 „	5 „	—	21 „
IV	270 „	70 „	13 „	44 „	27 „

In the last experiment scarcely any mercuric acetate remained unchanged.

As a rule, the crude monochloromercuri-*p*-nitrotoluene contained about 25% of matter insoluble in acetone. The purified products

were colourless solids, readily soluble in hot acetone and fairly easily soluble in hot glacial acetic acid, from which they separated in feathery or woolly crystals. In all cases, however, they were ill-defined and obviously mixtures. They consisted of pure monochloromercuri-*p*-nitrotoluenes (Found: Hg, 53·2, 52·9; Cl, 9·9; N, 3·8. $C_7H_6O_2NClHg$ requires Hg, 53·9; Cl, 9·5; N, 3·8%), but could not be separated into their components by crystallisation.

Orientation of the Chloromercuri-4-nitrotoluenes.—The mixture was very readily converted by an equivalent quantity of bromine, dissolved in potassium bromide solution, into a pale yellow oil consisting of the corresponding bromo-*p*-nitrotoluenes. This was distilled in steam and solidified on cooling. Crystallisation from alcohol furnished pure 2-bromo-4-nitrotoluene, m. p. 76°, in small yields, but it proved impossible to isolate pure 3-bromo-4-nitrotoluene by crystallising the oils and buttery solids which remained.

Differential Action of Bromine in Carbon Tetrachloride.—The crude product (24 g. from an experiment identical with II), suspended in 104 c.c. of dry carbon tetrachloride containing 10·4 g. of bromine, was kept in the dark for 12 weeks; bromine and unchanged chloromercuri-*p*-nitrotoluene were then still present. The solution was filtered, the solvent evaporated, and the yellow, buttery residue crystallised from methyl alcohol, about 3 g. of pure 2-bromo-4-nitrotoluene being obtained. The mercuric bromide produced and the unchanged substance were treated with bromine in potassium bromide solution; a further quantity of mixed bromonitrotoluenes was then obtained as an oil. This was distilled in steam; it solidified (m. p. 30—35°) after several weeks and on crystallisation from methyl alcohol gave 3 g. of very pale yellow, prismatic needles of 3-bromo-4-nitrotoluene, m. p. 36°. Hence the original mixture of monochloromercuri-4-nitrotoluenes must have contained at least 25% of the unexpected 3-compound.

2-*Bromo*-4-*nitrotoluene.*—A solution of *p*-nitro-*o*-toluidine (25 g.) in hydrobromic acid was diazotised and added to a cooled solution of cuprous bromide and the product was distilled in steam (compare Blanksma, *Chem. Weekblad*, 1909, **6**, 899), practically pure 2-bromo-4-nitrotoluene passing over (yield, 90%). After crystallising twice from alcohol, it was obtained in almost colourless, glistening needles; the fused solid froze constantly at 75·8°. In the literature, the melting point is variously given as from 75° to 78° (compare Nevile and Winther, *Ber.*, 1881, **14**, 418; Scheufelen, *Annalen*, 1885, **231**, 171).

*Nitration of Aceto-*m*-toluidide and Preparation of* 3-*Bromo*-4-*nitrotoluene.*—A solution of *m*-toluidine (15 g.; 2 mols.) in 90 g. of acetic anhydride was cooled to 0° and shaken with trihydrated copper

nitrate (16·4 g., recrystallised from hot concentrated nitric acid and carefully dried). The copper salt gradually dissolved with evolution of heat and the temperature was kept as low as possible by cooling in ice; copper acetate crystallised as the reaction proceeded. The main reaction was over in about 1½ hours and cooling was then unnecessary. After 12 hours, the mixture was poured into 3 litres of ice-water and stirred until the anhydride had disappeared. The washed yellow solid (21 g.; m. p. 58—68°), which was free from occluded copper salts, was crystallised from alcohol (good cooling was required to crystallise the 4-nitro-compound), 4-nitroaceto-*m*-toluidide separating in long sheaves of golden-yellow needles and 6-nitroaceto-*m*-toluidide in compact, crimson prisms. The two compounds were separated mechanically and each was recrystallised until pure.

4-Nitroaceto-*m*-toluidide, thus obtained in long, golden needles, m. p. 85·8°, was warmed on a water-bath with 2½ times its weight of hydrobromic acid (*d* 1·4) and the solution was added to 40 c.c. of hydrobromic acid and 30 c.c. of water and cooled below 0°. The theoretical quantity of sodium nitrite dissolved in ten times its weight of water was then added all at once with violent agitation, and the clear diazotised solution added to a cooled solution of cuprous bromide obtained by boiling 3·5 parts of copper oxide and 5·2 parts of copper in 70 parts of hydrobromic acid (*d* 1·4) and 8 parts of water. A violent action took place and when this had subsided the bromonitrotoluene was distilled in steam. The yield was nearly theoretical. The oil solidified readily and was then recrystallised from methyl alcohol until the freezing point was constant. 3-Bromo-4-nitrotoluene crystallises in pale yellow prisms or needles, m. p. 36·2°.

The System 2-*Bromo*-4-*nitrotoluene*–3-*Bromo*-4-*nitrotoluene*.

The final melting points of mixtures of these two substances were determined by cooling the molten mixture very slowly with constant vigorous agitation until solidification began and then remelting by gentle warming, the temperature at which a solid phase ceased to exist being observed to within 0·1°. No untoward difficulties were encountered and the results were as follows:

2-Bromo-4-nitrotoluene %.	M. p.	2-Bromo-4-nitrotoluene %.	M. p.	2-Bromo-4-nitrotoluene %.	M. p.	2-Bromo 4-nitrotoluene %.	M. p.
—	36·2°	24·4	25·4°	44·75	39·2°	70·65	59·6°
3·57	35·0	29·75	22·6	49·55	43·6	77·1	63·7
7·34	33·3	32·1	25·6	53·9	47·4	89·2	70·6
12·6	31·2	37·0	31·8	57·35	50·2	100·0	75·8
17·1	29·0	41·3	36·0	64·6	56·0		

Mixtures containing from 17·1 to 37% of 2-bromo-4-nitrotoluene, on being cooled continuously below the solidification point, solidified completely when the eutectic temperature, 22·2°, was reached.

Quantitative Results obtained on mercurating p-*Nitrotoluene.*

The above melting points were used to determine the composition of the mixtures of monochloromercuri-4-nitrotoluenes obtained by mercurating *p*-nitrotoluene. The mixture was converted quantitatively into a mixture of the corresponding bromonitrotoluenes by treatment with bromine in potassium bromide solution and the bromonitrotoluenes were distilled in steam, filtered off while still warm and liquid through a wet filter, and dried. The melting points of these mixtures were then determined.

The mixture of chloromercuri-*p*-nitrotoluenes obtained in Expt. III gave a mixture of bromonitro-compounds melting completely at 22·8°; addition of a small quantity of pure 2-bromo-4-nitrotoluene raised the melting point. The mixture also solidified completely at the eutectic point—which was a clear proof of its being a mixture of the two bromonitrotoluenes. It therefore contained 30·5% only of the normal substitution product, namely, 2-bromo-4-nitrotoluene, and 69·5% of 3-bromo-4-nitrotoluene.

The mixture obtained in Expt. IV by heating for 13 hours gave a mixture melting at 26·4°, the solid phase being the 3-bromo-compound. This corresponds to 22·5% of the normal substitution product and 77·5% of the compound substituted in the 3-position.

Synthesis of 2-Chloromercuri-4-nitrotoluene.

4-Nitrotoluene-2-sulphonic acid was prepared by heating 50 g. of *p*-nitrotoluene and 110 g. of 20% oleum at 120° for 2 hours. The mixture was poured into 500 c.c. of saturated potassium chloride solution and the potassium salt was filtered off and recrystallised from water with the aid of charcoal (yield of anhydrous salt, 70%; compare Beilstein and Kuhlberg, *Annalen*, 1870, **155**, 8; Janssen, *ibid.*, 1874, **172**, 230).

4-*Nitrotoluene-2-sulphinic Acid.*—The molten sulphonyl chloride (10 g.; prepared from the potassium salt in the usual way) was shaken with a solution of 10·5 g. of sodium sulphite in 25 c.c. of water, the acidity that developed being corrected by the occasional addition of 50% caustic soda solution (total amount of caustic soda required, 3·3 g. or 2 mols.). Eventually the mixture reached a temperature of 65° and all the sulphonyl chloride disappeared; the whole mass then suddenly crystallised. The *sodium* salt was collected when cold and dried in a desiccator over-night (yield,

7 g.) (Found: Na, 9·1; H_2O, 13·9. $C_7H_6O_4NSNa,2H_2O$ requires Na, 8·9; H_2O, 13·9%).

4-Nitrotoluene-2-sulphinic acid, prepared by acidifying an aqueous solution of the sodium salt, slowly separated in shining, pale yellow plates, m. p. 127—128°. It was fairly stable in air but reduced permanganate (Found, by oxidation with permanganate: *M*, 199·2. Calc.: *M*, 201). The ferric salt was prepared (Found: Fe, 8·8. Calc.: Fe, 8·3%).

2-Chloromercuri-4-nitrotoluene was obtained as a white solid when the sulphinic acid was boiled with a 50% aqueous alcoholic solution of mercuric chloride. The solid was washed with 50% alcohol, dried, and extracted with acetone. From the extract, 2-chloromercuri-4-nitrotoluene separated in feathery needles, m. p. 230—231° (corr.).

Synthesis of 3-*Chloromercuri*-4-*nitrotoluene.*

Sulphonation of p-*Nitro*-o-*toluidine.*—The nitrotoluidine was mixed with chlorosulphonic acid (1½ mols.) and heated very cautiously to 150°. A fairly vigorous reaction took place, which was at an end in about an hour. (If the heating is not properly controlled, a vigorous reaction takes place with explosive violence and much charring.) The solid mass was dissolved in dilute boiling aqueous ammonia; the filtered solution, on cooling, deposited a mixture of four-sided plates and yellow needles. The latter (unchanged base) were removed by washing the mixture with ether, and the plates were then recrystallised from hot water, giving large, golden, striated, four-sided, anhydrous tablets of *ammonium* 4-*nitro*-2-*aminotoluene*-5-*sulphonate* (Found: NH_3, 6·8. $C_7H_{11}O_5N_3$ requires NH_3, 6·8%).

The *potassium* salt was similar in appearance and general properties. The *sulphonic acid*, prepared from the ammonium salt, crystallised in colourless needles with no definite melting point. The ammonium salt was dissolved in hot hydrochloric acid and reduced with the calculated quantity of stannous chloride, 2 : 4-tolylenediamine-5-sulphonic acid being formed in almost theoretical yield. The properties of this acid and of its potassium and barium salts and hydrochloride agreed almost exactly with the descriptions given by Foth (*loc. cit.*).

4-*Nitrotoluene*-2-*diazonium*-5-*sulphonate.*—A fine suspension of ammonium 4-nitro-2-aminotoluene-5-sulphonate (16·5 g.) in water was treated in the cold with 10 g. of sodium nitrite (in water) followed by an excess of dilute sulphuric acid. The white, crystalline substance produced was collected after 12 hours, well washed, and dried in the air (yield, theoretical). The compound was very sparingly soluble and exploded on heating.

4-*Nitrotoluene*-3-*sulphonic Acid*.—The diazonium compound was suspended in six times its weight of formic acid (*d* 1·2), and 4 g. of copper powder were added. Nitrogen was evolved immediately and, on warming, a violent evolution of nitrogen and carbon dioxide (1·4 : 1·0) took place. A blue solution was produced—this and the low production of carbon dioxide point to the fact that the copper plays some part in the oxidation of the formic acid. Water was then added, the solution boiled and filtered, the formic acid distilled in steam, and the copper removed as sulphide. The acid solution was then neutralised with barium carbonate and evaporated. (The author is indebted to Dr. Brady for suggesting this method of removing the diazonium group.) The *barium* salt was extremely soluble and could only be obtained as a viscous syrup. The *potassium* salt, prepared from the barium salt, was obtained as a very soluble, pale yellow, anhydrous, crystalline powder (yield, 10 g. from 16 g. of the diazonium compound) (Found : K, 15·2. $C_7H_6O_5NSK$ requires K, 15·3%).

The sulphonyl chloride was obtained, by the action of phosphorus pentachloride on the above salt, as a pale brown oil which would not crystallise.

4-*Nitrotoluene*-3-*sulphinic Acid*.—The sulphonyl chloride was treated with sodium sulphite and caustic soda in the way previously described for the preparation of 4-nitrotoluene-2-sulphinic acid. The reaction was difficult to control satisfactorily. The dark brown solution was filtered from tar, diluted to 200 c.c., acidified, filtered hot through a wet filter, cooled, and treated with ferric chloride, and the sparingly soluble ferric salt was collected. This was converted into the ammonium salt, and the solution evaporated to small bulk and acidified; the sulphinic acid then separated as an oil, which formed colourless crystals, m. p. 112—113°, on scratching (yield, 1·5 g.) (Equiv. : found, 202; calc., 201).

3-*Chloromercuri*-4-*nitrotoluene*.—The sulphinic acid reacted readily with mercuric chloride in boiling 50% alcohol. The solid obtained was filtered off, washed, and extracted with hot acetone, almost all of it dissolving. The solution was boiled with charcoal and allowed to crystallise, 3-*chloromercuri*-4-*nitrotoluene* separating as a felty pad of very small, colourless needles, m. p. 226—227° (corr.). This compound does not crystallise so beautifully as its isomeride and is identical in appearance with the crude mercuration product. Crystallisation from acetic acid did not alter its melting point (Found : Hg, 54·4%). On treatment with bromine in potassium bromide solution this compound furnished pure 3-bromo-4-nitrotoluene, m. p. 36°.

Mercuration of m-*Nitrotoluene.*

m-Nitrotoluene (m. p. 15·5°; purified by freezing) (500 g.) was heated with mercuric acetate (125 g.), with occasional shaking, at 120—130° for 1 hour and then at 130—140° for 12 hours until a test portion of the mixture no longer gave a precipitate of mercuric oxide when treated with cold sodium hydroxide solution. When cold, the liquid was filtered from 9 g. of solid matter and poured into 6 litres of ether; about 10 g. of polymercurated nitrotoluenes then separated. The ether was distilled and the residual *m*-nitrotoluene solution was treated with brine and distilled in steam. When about half of the excess of nitrotoluene had been removed a large amount of solid (82 g.) separated and distillation became difficult. The remaining nitrotoluene was therefore decanted and again distilled in steam until the separation of more solid made distillation impossible. The combined solids were boiled with water until free from occluded nitrotoluene. The crude product (105 g.) was found by analysis to consist only of monochloromercurinitrotoluenes.

The aqueous solution in the distillation flask contained mercuric salts equivalent to 5 g. of mercuric acetate.

5-*Chloromercuri*-3-*nitrotoluene.*—The crude chloromercuri-*m*-nitrotoluenes were boiled with 300 c.c. of acetone for ½ hour, and the mixture filtered hot. The insoluble portion (20 g.) was extracted with hot acetone (three lots of 200 c.c. each). 5-*Chloromercuri*-3-*nitrotoluene* remained undissolved; it melted at 294° (corr.), even after recrystallisation from glacial acetic acid. It crystallised in colourless, feathery needles (Found: Hg, 53·3. $C_7H_6O_2NClHg$ requires Hg, 53·9%).

When treated with bromine in carbon tetrachloride or potassium bromide solution, the compound gave a theoretical yield of bromonitrotoluene, m. p. 80—81·5°, which crystallised from methyl alcohol in pale yellow needles, m. p. 83·5—84·5° (corr.). 5-Bromo-3-nitrotoluene, which has the highest melting point of all the known bromo-*m*-nitrotoluenes, melts at 81·4—81·8° (Nevile and Winther, *Ber.*, 1880, **13**, 969).

4-*Chloromercuri*-3-*nitrotoluene.*—The acetone extracts obtained above, on cooling, deposited a mixture containing small clusters of well-defined crystals. These were separated mechanically and crystallised from acetone until the m. p. remained constant. 4-*Chloromercuri*-3-*nitrotoluene* was thus obtained in clusters of pale yellow needles resembling mimosa flowers, m. p. 210° (corr.; sintering at 207°).

The substance obtained by treating this compound with bromine

in potassium bromide solution (yield, quantitative) melted at 32—33° and on crystallisation from methyl alcohol furnished 4-bromo-3-nitrotoluene, m. p. 35°, identical with a specimen obtained from 3-nitro-*p*-toluidine (compare Beilstein and Kuhlberg, *Annalen*, 1871, **158**, 344; Nevile and Winther, *loc. cit.*; Claus, *J. pr. Chem.*, 1892, **46**, 25).

Presence of 6-Chloromercuri-3-nitrotoluene.—The remainder of the chloromercuri-*m*-nitrotoluenes was converted quantitatively into a mixture of bromonitrotoluenes by means of bromine in potassium bromide solution. This mixture was reduced to the corresponding amino-compounds by warming it on a water-bath with three times its weight of hydrated stannous chloride in concentrated hydrochloric acid for 2½ hours. The solution was then almost neutralised with sodium hydroxide solution, and an excess of sodium acetate added. The weakly acid solution on distillation with steam furnished a mixture of bromotoluidines which could not be crystallised. The residue in the distillation flask was made alkaline with sodium hydroxide and distilled with steam; the oil in the distillate rapidly solidified and after being dried on tile it crystallised from 50% alcohol in colourless plates, m. p. 79·5—80° (corr.). Since all the other known bromo-*m*-toluidines melt below 40°, the substance must be 6-bromo-*m*-toluidine (compare Scheufelen, *Annalen*, 1885, **231**, 180, who gives the m. p. as 78°). Thus 6-chloromercuri-3-nitrotoluene was present in the product of mercuration of *m*-nitrotoluene.

The remaining bromotoluidines were acetylated and the mixture obtained was recrystallised several times from alcohol, but only a small quantity of 4-bromoaceto-*m*-toluidide, m. p. 164°, could be isolated.

The author wishes to express his thanks to Professor J. N. Collie for the facilities afforded him, and also to the Trustees of the Ramsay Memorial Trust for the grant of a fellowship.

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LONDON, W.C.1. [*Received, August 28th*, 1926.]

CCCCXXXV.—*Studies in Optical Superposition. Part VII. The Bornyl Dimethoxysuccinates.*

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IN previous parts of this investigation (see J., 1924, **125**, 2579), attempts have been made to test the validity of van 't Hoff's principle of optical superposition by the only method which, as far

as can be seen at present, may be expected to give the least equivocal results.*

As a further test of the validity of van 't Hoff's assumption, we have prepared the bornyl esters of *d*-, *l*-, and *meso*-dimethoxysuccinic acid with the object of comparing the mean value of the specific rotations for the former two substances with the specific rotation found for the third. If the principle holds accurately, these values should always be identical. Nevertheless it ought to be noted that even a complete agreement is not necessarily a proof of the validity of the principle. As has been shown already (J., 1915, **107**, 145), it would be possible, even in the event of complete agreement, for the so-called principle to be violated.

Bornyl l-*dimethoxysuccinate* was prepared by passing dry hydrogen chloride into a mixture of 10 g. of methyl *l*-dimethoxysuccinate (m. p. 51°; obtained by Patterson and Patterson's method, J., 1915, **107**, 142) with 60 g. of borneol for 1 hour at the ordinary temperature, partial liquefaction taking place (compare Patterson and Dickinson, J., 1901, **79**, 280), and then for 24 hours at 100°. In the operation, sublimation of the borneol causes difficulty. The product was distilled under reduced pressure after removal of excess borneol at a lower temperature. The fraction, b. p. about 265°/15 mm., consisted of 6 g. of fairly pure ester, readily soluble in organic solvents. The *ester*, after four crystallisations from 75% aqueous alcohol, had m. p. 70° and $\alpha_g^{14°}$ (100 mm.) constant at −2·28° (Found : C, 69·1; H, 9·4. $C_{26}H_{42}O_6$ requires C, 69·3; H, 9·3%).

Bornyl d-*dimethoxysuccinate* was prepared and purified in a similar manner. The m. p. rose from 100° to 103° after four crystallisations from aqueous alcohol and $\alpha_g^{16°}$ (100 mm.) became constant at + 11·4°. The ester is easily soluble in the common organic solvents (Found : C, 69·2; H, 9·3%).

Bornyl i-*dimethoxysuccinate* was prepared from *i*-dimethoxysuccinic acid (m. p. 162°), which was obtained by hydrolysis of the methyl ester. The acid (10 g.) was mixed with 60 g. of borneol and the same procedure followed as before. This ester is much less soluble than the other two in alcohol, but is readily soluble in most common organic solvents. After seven crystallisations from aqueous alcohol the m. p. was 114° and $[\alpha]_g^{12·5°}$ +44·79° ($c = 0·855$) (Found : C, 69·5; H, 9·4%).

These esters were examined, not in the homogeneous condition on

* Hudson also (*J. Amer. Chem. Soc.*, 1924, **46**, 462, 979, 2591; 1925, **47**, 265, 537, 873, 2052; and other papers) has been carrying out work which involves this principle. Since it seems to us, however, that the criticism of Hudson's work which was made in Part VI (*loc. cit.*) applies in a similar manner to his later work, we shall not again refer to it here.

account of their rather high melting points, but at similar concentration in five different solvents, for three colours of light and over a range of temperature. The experimental data will be found at the end of the paper. Table I summarises the results with regard to the main point under investigation.

TABLE I.

Specific rotation of bornyl esters of dimethoxysuccinic acids.

Solvent.	t.	c.	I. d-Ester.	II. l-Ester.	III. i-Ester.	IV. Mean of I and II.	Δ IV−III.
Alcohol	0°	4·5	131·0°	−37·9°	44·7°	46·55°	1·85°
	20		126·0	−35·3	43·5	45·35	1·85
Pyridine	0	5	141·3	−55·9	37·1	42·7	5·6
	20		134·5	−52·6	36·5	40·95	4·45
Benzene	20	5	127·4	−45·5	39·2	40·95	1·75
Chloroform	0	5	128·6	−28·1	50·65	50·25	−0·4
	22		121·8	−26·45	48·0	47·7	−0·3
Ethylene dibromide	20	7	130·9	−26·2	49·2	52·35	3·15

If the hypothesis of van 't Hoff regarding optical superposition be correct, the mean of the rotations of the d- and l-forms should have the same value as that of the ester of the i-acid. It will be seen that this is nearly so in this series of compounds. Nevertheless the following points are to be noticed :

(1) That in each solvent for which observations are quoted for two temperatures the differences are in the same sense, which would seem to show that the differences are not due to experimental error.

(2) That the differences are not the same in the various solvents used seems also to favour the view that our results are not due to any constant error such as impurity of one or more of the esters used, but are really due to invalidity of the principle.

(3) The effect of change of temperature upon these differences seems to us to be significant. Table II shows the data for these three esters dissolved in chloroform and in alcohol, values in the latter case being taken from smoothed temperature–rotation curves.

TABLE II.

Variation of Δ with change of temperature.

In chloroform	$t°$	0	22	44·8	
	Δ	−0·40	−0·28	+0·36	
In alcohol	$t°$	0	20	40	60
	Δ	1·8	1·6	1·2	0·3

In chloroform, the difference which at first was negative became less so as the temperature increased and changed into a positive value at higher temperatures. The difference in the case of alcohol

diminished gradually as the temperature rose. It thus appears that in chloroform one could realise a condition of affairs in which the difference would be zero and van 't Hoff's principle would hold completely in these particular circumstances. Although this temperature is not actually reached in alcohol, it also might be realised. The fact that the differences observed in experiments such as ours is dependent upon the temperature in this way seems to us to indicate that van 't Hoff's supposition cannot be regarded as a general principle, especially since, although in some cases such as those presently recorded the agreement of the experimental data with the requirements of the principle is close, in other cases, *e.g.*, the secondary octyl esters of the tartaric acids (J., 1924, **125**, 1476) and their menthylamine salts (*ibid.*, 1915, **107**, 142), the difference is very considerable.

[*Note added*, 11*th October*, 1926.] Some time after this paper had been sent in for publication Professor A. McKenzie directed our attention to the fact that commercial borneol was liable to contain *l-iso*borneol, and this we found in the sample we had used. Its rotation had been determined for various colours of light, but the fact that this was too low had been overlooked. Therefore, as a crucial test of the purity of the esters at this late stage, we decided to recover the borneol by hydrolysis from the specimens we still had left, but as we had only a small quantity of each (about 0·4 g.), we mixed together * approximately that amount of each ester and hydrolysed the mixture with alcoholic potash. After neutralisation, the borneol was extracted with ether, the solution dried with potassium carbonate, and the ether distilled off. The addition of a few drops of alcohol and water brought about the separation of the borneol. This was filtered off and dried. The melting point of the substance thus obtained, without recrystallisation, was 205° (uncorr.) and 208·7° (corr.). Its rotation was examined in alcoholic solution at 19·5° in a 100 mm. tube ($c = 12·268$).

λ	5892	5792	5461	4358
	D.	Hg_{γ}.	Hg_{g}.	Hg_{ν}.
α	+4·62°	4·75°	5·475°	9·34°
$[\alpha]$	37·7°	38·7°	44·6°	76·1°

Haller (*Ann. Chim. Phys.*, 1892, **27**, 394) gives for alcohol ($c = 15·4$, $t = 10$—$15°$), $[\alpha]_D = +37·33°$. Pickard and Littlebury (J., 1907, **91**, 1978) give + 37·08° and + 37·03° for solutions in alcohol of about the same concentration.

It appears, therefore, that the borneol recovered from these

* The total quantity of borneol recovered was just over 0·6 g. Had each ester been hydrolysed separately, the quantity of borneol obtained from each would, we were afraid, have been too small for accurate polarimetric measurement.

esters was quite pure and this seems to be very sound evidence that the esters themselves were pure.

We also recovered the *d*-bornyl *l*-dimethoxysuccinate from its solutions in pyridine and ethylene bromide, which had been used in the polarimetric experiments, and separated the borneol as above. Only 0·2822 g. was obtained which had m. p. 202—203° and gave $\alpha^{16°}_{5461} = +2{\cdot}44°$, whence $[\alpha]^{16°}_{5461} = 43{\cdot}3°$. Considering the smallness of the quantity at our disposal and that it could not be purified, this value agrees as closely as could be expected with the other.

For still further confirmation, we prepared a fresh specimen of *d*-bornyl *d*-dimethoxysuccinate from *d*-dimethoxysuccinic acid and *d*-borneol purified by boiling in benzene solution with zinc chloride (Pickard and Littlebury, *loc. cit.*), the rotation having thus been raised from $[\alpha]_{5461} = 34{\cdot}28°$ to $[\alpha]_{5461} = 43{\cdot}49°$ ($c = 12{\cdot}268$ in alcohol). After crystallisation from aqueous alcohol, this melted at 104° and had, in benzene solution, $\alpha^{20°}_{5461}$ (154·1 mm.) $= +9{\cdot}79°$, whence $[\alpha]^{20°}_{5461} = +128{\cdot}07°$, the value previously found being 127·42°.

Further, *l*-bornyl *i*-dimethoxysuccinate was prepared afresh from methyl *i*-dimethoxysuccinate and natural *l*-borneol of $\alpha_{5461} = -43{\cdot}04°$ ($c = 12{\cdot}268$ in alcohol). After one crystallisation from aqueous alcohol, the ester softened at 105° and melted at 113—114°. In benzene ($c = 5$), $\alpha^{20°}_{5461}$ (154·1 mm.) $= -2{\cdot}97°$, whence $[\alpha]^{20°}_{5461} = -39{\cdot}0°$, the value previously found being −39·2°.

It seems clear, therefore, that the processes of purification to which our original preparations had been subjected had eliminated the influence of any *l-iso*borneol present in the borneol used.

Experimental.

The solvents were all carefully purified before use.

The wave-lengths of the light used were 5790·3, 5460·7, and 4358·3 and, to save space, are denoted throughout by the letters *y*, *g*, and *v*, respectively.

The solutions of the three esters were prepared as nearly as possible of the same strength, and were examined under similar conditions.

Bornyl *d*-dimethoxysuccinate in ethylene dibromide.

Densities det. : 2·0963/12·3°, 2·0475/37°, 2·0058/57·1°, 1·9725/74·6°, 1·9231/98·5°. $p = 3{\cdot}3518$.

t.	a_y.	a_g.	a_v.
20°	12·27°	14·07°	23·18°
45·5	11·32	12·99	21·31
73	10·59	11·94	19·17
99·7	9·74	11·07	17·37

Bornyl *d*-dimethoxysuccinate in chloroform.

Densities det. : 1·4649/13°, 1·4449/25°, 1·4110/43·4°. $p = 3{\cdot}4310$.

t.	a_y.	a_g.	a_v.
0°	8·76°	10·11°	16·66°
22	8·24	9·34	15·34
44·7	7·68	8·78	14·40

Bornyl *d*-dimethoxysuccinate in benzene.

Densities det.: 0·8947/10°, 0·8714/32°, 0·8470/58°. $p = 5·6115$.

t.	a_y.	a_g.	a_v.
20°	8·34°	9·74°	16·27°
39·2	7·93	9·21	15·22
57	7·67	8·78	14·38

Bornyl *d*-dimethoxysuccinate in alcohol.

Densities det.: 0·8088/12·2°, 0·7892/36°, 0·7808/45·5°, 0·7698/58°. $p = 5·5774$.

t.	a_y.	a_g.	a_v.
0°	8·13°	9·22°	15·15°
20	7·65	8·69	14·35
38·8	7·23	8·17	13·55
54	6·86	7·77	12·91

Bornyl *d*-dimethoxysuccinate in pyridine.

Densities det.: 0·9908/14°, 0·9738/31·6°, 0·9553/50·3°. $p = 5·0458$.

t.	a_y.	a_g.	a_v.
0°	9·56°	11·03°	18·01°
20	9·04	10·30	16·92
44·2	8·47	9·52	15·68

Bornyl *l*-dimethoxysuccinate in ethylene dibromide.

Densities det.: 2·0980/11°, 2·0481/37°, 1·9982/61·5°, 1·9668/78°, 1·9241/98°. $p = 3·3511$.

t.	a_y.	a_g.	a_v.
20°	−2·49°	−2·82°	−4·31°
44·3	2·27	2·57	3·83
73·8	1·95	2·22	3·23
99·5	1·69	1·98	2·66

Bornyl *l*-dimethoxysuccinate in chloroform.

Densities det.: 1·4585/17·8°, 1·4378/30°, 1·4120/44°. $p = 3·4315$.

t.	a_y.	a_g.	a_v.
0°	−1·86°	−2·21°	−3·30°
22	1·67	2·03	3·07
44·7	1·60	1·93	2·80

Bornyl *l*-dimethoxysuccinate in benzene.

Densities det.: 0·8814/24°, 0·8669/38·2°, 0·8463/57·7°. $p = 5·6116$.

t.	a_y.	a_g.	a_v.
20°	−3·08°	−3·48°	−5·64°
38·7	2·89	3·25	5·25
56·5	2·70	3·05	4·95

Bornyl *l*-dimethoxysuccinate in alcohol.

Densities det.: 0·8099/14·7°, 0·8006/26·7°, 0·7887/40·6°, 0·7767/53·7°. $p = 5·5874$.

t.	a_y.	a_g.	a_v.
0°	−2·19°	−2·68°	−4·16°
20	2·00	2·45	3·87
39·4	1·83	2·25	3·51
55	1·69	2·09	3·27

Bornyl *l*-dimethoxysuccinate in pyridine.

Densities det.: 0·9892/15°, 0·9724/32·5°, 0·9551/50°. $p = 5·0482$.

t.	a_y.	a_g.	a_v.
0°	−3·79°	−4·36°	−6·85°
20	3·53	4·03	6·31
45·5	3·17	3·59	5·65

Bornyl *i*-dimethoxysuccinate in ethylene dibromide.

Densities det.: 2·0922/13°, 2·0503/33·7°, 2·0057/56·7°, 1·9680/75·5°, 1·9188/98·5°. $p = 3·3382$.

t.	a_y.	a_g.	a_v.
20°	4·72°	5·26°	8·95°
43·7	4·41	4·95	8·51
73	4·09	4·59	8·03
99	3·86	4·37	7·41

Bornyl *i*-dimethoxysuccinate in chloroform.

Densities det.: 1·4590/17°, 1·4339/32°, 1·4116/44°. $p = 3·4282$.

t.	a_y.	a_g.	a_v.
0°	3·52°	3·98°	6·63°
22	3·23	3·69	6·15
44·8	3·10	3·40	5·80

Bornyl *i*-dimethoxysuccinate in benzene.

Densities det.: 0·8859/20·5°, 0·8663/39·1°, 0·8496/55°. $p = 5·5854$.

t.	a_y.	a_g.	a_v.
20°	2·69°	2·99°	4·98°
39	2·54	2·87	4·84
56	2·46	2·79	4·72

Bornyl *i*-dimethoxysuccinate in alcohol.

Densities det.: 0·8037/17·6°, 0·7916/31·8°, 0·7800/45·5°, 0·7689/58°. $p = 5·5830$.

t.	a_y.	a_g.	a_v.
0°	2·84°	3·15°	5·38°
20	2·70	3·00	5·08
38·5	2·55	2·89	4·82
54·2	2·41	2·80	4·61

Bornyl *i*-dimethoxysuccinate in pyridine.

Densities det.: 0·9883/15·7°, 0·9703/34·5°, 0·9522/52·3°. $p = 5·0453$.

t.	a_y.	a_g.	a_v.
0°	2·53°	2·89°	4·76°
20	2·45	2·79	4·63
44·6	2·30	2·64	4·45

Our thanks are due to the Carnegie Trustees for the Universities of Scotland for grants which partly defrayed the expenses of this investigation.

UNIVERSITY OF GLASGOW. [*Received, April 29th*, 1926.]

CCCCXXXVI.—*The Decomposition of Substituted Carbamyl Chlorides by Hydroxy-compounds. Part III. The Influence of Substituent Groups.*

By TUDOR WILLIAMS PRICE.

THE reaction between phenylmethylcarbamyl chloride and ethyl alcohol at various temperatures has already been studied (J., 1924, **125**, 115). An account is now given of the reaction between ethyl alcohol and other substituted carbamyl chlorides at 100°.

Materials.—All the substituted carbamyl chlorides used, with the exception of the diphenyl compound, which was obtained from Kahlbaum, were prepared by passing carbonyl chloride through a benzene solution of the requisite secondary amine. After removal of any unchanged amine and of hydrogen chloride and benzene, the product was purified by several distillations under reduced pressure, if a liquid, or by repeated crystallisation from light petroleum, if a solid.

Phenyl-n-propylcarbamyl chloride was prepared by passing carbonyl chloride into a solution of *n*-propylaniline (30 g.) in benzene (150 c.c.), cooled by ice-cold water, until the solution was saturated. The solution, which now contained *n*-propylaniline hydrochloride in

suspension, was washed with water, dried, and evaporated, leaving 13 g. of crude *phenyl*-n-*propylcarbamyl chloride*. This crystallised from light petroleum in colourless, short prisms (6 g.), m. p. 45·5—46°. The compound has a penetrating but not unpleasant odour and is easily soluble in alcohol, ether, chloroform, benzene, ethyl acetate, or acetone, but insoluble in water (Found: Cl, 17·8. $C_{10}H_{12}ONCl$ requires Cl, 18·0%).

*Phenyliso*propylcarbamyl chloride, similarly prepared from *iso*propylaniline, crystallised from light petroleum in colourless prisms, m. p. 90—90·5°. It is very soluble in alcohol, ether, chloroform, benzene, or acetone, but insoluble in water, and has a penetrating odour similar to that of the *n*-propyl compound (Found: Cl, 17·9%).

Phenyl-n-*butylcarbamyl chloride*, obtained from *n*-butylaniline, is a pungent, colourless liquid, b. p. 165—166°/20 mm., miscible in all proportions with alcohol, ether, benzene, and other organic solvents, but insoluble in water (Found: Cl, 16·7. $C_{11}H_{14}ONCl$ requires Cl, 16·8%).

Phenylisobutylcarbamyl chloride, b. p. 149—151°/19 mm., resembles the *n*-butyl compound in its physical properties (Found: Cl, 16·6%).

Phenylisoamylcarbamyl chloride, obtained from *iso*amylaniline, is a colourless liquid, b. p. 153—153·5°/10 mm., with a strong, sweet odour; it is miscible in all proportions with alcohol, ether, benzene, or acetone, but insoluble in water (Found: Cl, 15·7. $C_{12}H_{16}ONCl$ requires Cl, 15·7%).

o-*Tolylethylcarbamyl chloride* was prepared from ethyl-*o*-toluidine and repeatedly crystallised from light petroleum. The colourless, short prisms, m. p. 36·5—37°, obtained were easily soluble in alcohol, ether, benzene, or chloroform, but insoluble in water, and had a sweet odour (Found: Cl, 17·9. $C_{10}H_{12}ONCl$ requires Cl, 18·0%).

The Reactions between Ethyl Alcohol and the Substituted Carbamyl Chlorides.

The ethyl alcohol was commercial absolute alcohol which had been treated twice at the boiling point with fresh calcium turnings (1·0 and 0·5% by weight) and fractionated. It distilled sharply at 78·6°.

The method of working was that described in Part I, section C (*loc. cit.*, p. 118), and the velocity coefficient of the reaction was calculated in each case from a knowledge of the amount of unchanged carbamyl chloride left in the system at any given time by means of the expression $k = 1/(t_2 - t_1) \cdot \log_e\{(a - x_1)/(a - x_2)\}$, where t_1 is 5 minutes after insertion of the tube into the bath kept at 100°.

In each experiment, a weight of carbamyl chloride equivalent to 25 c.c. of $N/10$-solution was dissolved in 5 c.c. of absolute alcohol.

Results.—In Table I, where the results for phenylethyl- and phenyl-*n*-propyl-carbamyl chloride are given in detail, the first column gives the duration of heating in minutes (t), the second the amount of hydrogen chloride present, expressed as c.c. of $N/10$-solution (b), and the third the amount of hydrogen chloride plus carbamyl chloride present, expressed as c.c. of $N/10$-solution (c). The fourth column gives the amount of carbamyl chloride present, also expressed as c.c. of $N/10$-solution (d) and obtained by subtracting the figures in column 2 from those in column 3. The fifth column gives the velocity coefficient for the reaction, calculated from the figures in column 4.

The whole of the results are summarised in Table II.

TABLE I.

Phenylethylcarbamyl chloride.					Phenyl-*n*-propylcarbamyl chloride.				
t.	b.	c.	d.	k.	t.	b.	c.	d.	k.
5	5·11	24·77	19·66	—	5	4·03	24·84	20·81	—
10	10·30	24·48	14·18	0·0655	8	6·92	24·79	17·87	0·0508
15	13·61	24·05	10·44	0·0633	10	8·59	24·48	15·89	0·0540
20	15·74	23·33	7·59	0·0634	13	10·62	24·23	13·61	0·0531
25	16·76	22·49	5·73	0·0617	15	11·83	24·10	12·27	0·0528
30	17·25	21·47	4·22	0·0617	20	13·98	23·53	9·55	0·0519
35	17·45	20·45	3·00	0·0627	25	15·40	22·56	7·16	0·0534
			Mean	0·0631				Mean	0·0527

TABLE II.

Carbamyl chloride.	Limits of k.	Mean k.
Phenyl-methyl	0·0437 —0·0417	0·0427
,, ethyl	0·0655 —0·0617	0·0631
,, *n*-propyl	0·0540 —0·0508	0·0527
,, *iso*propyl	0·223 —0·210	0·215
,, *n*-butyl	0·0550 —0·0540	0·0545
,, *iso*butyl	0·0297 —0·0280	0·0290
,, *iso*amyl	0·0422 —0·0403	0·0414
,, benzyl	0·0217 —0·0209	0·0214
Diphenyl	0·00128—0·00115	0·00123
o-Tolylethyl	0·0396 —0·0362	0·0376

The experiments with phenylmethyl-, phenylethyl-, phenyl-*n*-propyl-, and phenyl-*n*-butyl-carbamyl chloride were repeated with the following results for the respective mean velocity coefficients : 0·0430, 0·0635, 0·0529, 0·0550.

The results in Table II show that so far as the compounds containing a straight-chain alkyl radical are concerned, the reactivity of the carbamyl chloride with ethyl alcohol, as measured by the ease with which the chlorine atom is removed, does not vary regularly with the weight of the alkyl radical. The order of reactivity (denoting the compound by the alkyl radical which is attached to

the nitrogen atom) is ethyl>*n*-butyl>*n*-propyl>methyl, a pronounced alternation in the value of the velocity coefficient being observed. This behaviour is not exceptional, having been found with other homologous series. Thus Crocker (J., 1907, **91**, 593), in the hydrolysis of aliphatic amides by hydrochloric acid, found an alternation in the bimolecular velocity coefficient in passing from formamide to butyramide. Crocker and Lowe, however (*ibid.*, p. 952), found no corresponding alternation when the same amides were hydrolysed by alkalis, the velocity coefficient decreasing as the weight of the alkyl radical increased. Clarke (J., 1910, **97**, 416) found an alternation in the reactivity of bromoacetic esters with pyridine in alcoholic solution, the bimolecular velocity coefficients being in the order ethyl>methyl>*n*-butyl>*n*-propyl ester.

For the branched-chain compounds a similar alternation is found, the reactivity being in the order *iso*propyl>*iso*amyl>*iso*butyl. The value of the velocity coefficient for the phenyl-*iso*propyl compound is exceptionally high and is probably connected with the fact that this is the only compound examined in this series in which nitrogen is attached to a >CH– group.

The replacement of the methyl group in phenylmethylcarbamyl chloride by a phenyl group decreases the reactivity considerably, causing the diphenyl compound to be the least reactive of all those examined. The introduction of a phenyl group into the alkyl chain also lowers the reactivity, as shown by the figures for the velocity coefficients of phenylmethyl- and phenylbenzyl-carbamyl chlorides. The replacement of the phenyl group by the *o*-tolyl group decreases the reactivity, as shown by a comparison between the figures for the phenylethyl and *o*-tolylethyl compounds.

The author wishes to thank the Chemical Society for a grant from the Research Fund which has partly defrayed the cost of this investigation.

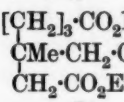
THE TECHNICAL COLLEGE, BRADFORD. [*Received, October 12th*, 1926.]

CCCCXXXVII.—*The Formation and Stability of Associated Alicyclic Systems. Part III. The Change from "Meta-" to "Para-" Bridged Rings.*

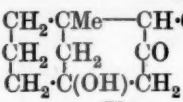
By ERNEST HAROLD FARMER and JOHN ROSS.

BY addition of esters to 1-methyl-Δ^1-*cyclo*hexen-3-one products of three types have been obtained. With ethyl sodiomalonate, the ketone yielded the ester (I) (Farmer and Ross, J., 1925, **127**, 2358),

with ethyl sodioacetoacetate the dicyclic ester (II) (Rabe, *Ber.*, 1904, **37**, 1671), and with methyl cyanoacetate and piperidine the ester (III) (Farmer and Ross, this vol., p. 1570). Evidence concerning



(I.)



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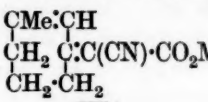
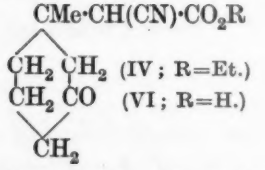


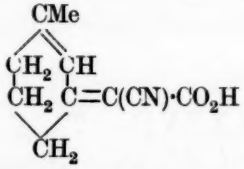
(III.)

the formation of (I) by successive stages of addition, "para-" bridging, and fission has been recorded in Part II of this series (*loc. cit.*). Thus not only is the type of ester addition to a Δ^1-*cyclo*hexenone determined by the mode of carrying out the reaction, but the subsequent formation of "meta-" or "para-" bridged rings from "Michael" addition products would appear to be controlled by the specific reactivity of the addendum towards the $\cdot CH_2 \cdot CO \cdot$ group of the ketone. The tendency, probably very diverse, to the formation of "meta" and "para" two-carbon bridges would then be compensated by differences in the nature of the added rings. On these grounds, it follows that where the addendum to the *cyclo*hexenone ring carries specific reactants for both methylene and carbonyl groups, as occurs with ethyl cyanoacetate, the type of bridged-ring produced depends on the conditions which exist during the initial addition. The stability of the bridged structures must, owing to their greatly differing constitutions, vary enormously. Working on this basis, we have been able to identify the numerous products derived directly and indirectly by the addition of ethyl sodiocyanoacetate to methyl*cyclo*hexenone.

The condensation product obtained by heating an alcoholic solution of the sodio-ester with the ketone gave ethyl methyl-*cyclo*hexanonecyanoacetate (IV) (21% yield), and a viscous acidic material from which crystals of methyl*cyclo*hexenylidenecyanoacetic acid * (V) separated. The ester (IV) gave the corresponding acid



(IV; R=Et.)
(VI; R=H.)

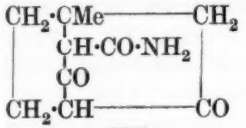


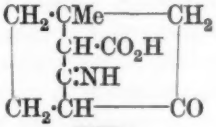
(V.)

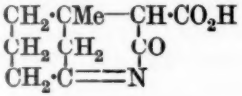
(VI) on hydrolysis with sodium carbonate; both yielded semicarbazones. Thus the neutral conditions existing during the additive reaction had inhibited further cyclisation.

* This acid represents a single geometrical form (maleinoid or fumaroid; m. p. 183°), whereas the ester obtained by condensation of methyl*cyclo*hexenone with ethyl cyanoacetate in the presence of piperidine is a mixture of both forms (acid, m. p. 149°) (Farmer and Ross, *loc. cit.*).

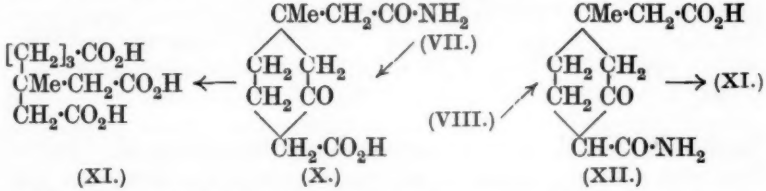
On short heating with hydrochloric acid, however, both ester (IV) and acid (VI) were quantitatively converted into a crystalline substance which gave an intense colour with ferric chloride and agreed in composition and basicity with the formulæ (VII) (enolic), (VIII), and (IX). Of these, (VII) and (VIII), derived by "Dieckmann" and "Thorpe" condensations, respectively, appear to be


(VII.)

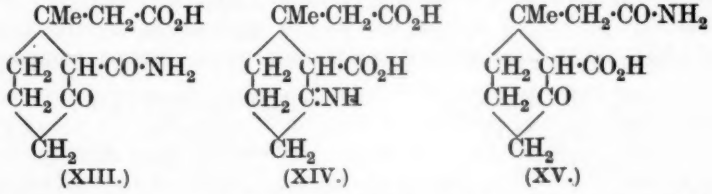

(VIII.)


(IX.)

excluded on the grounds of stability and unsuitability of the condensing agent. On the other hand, prolonged boiling with caustic alkali caused quantitative conversion of the crystalline substance into the open-chain acid (XI)—a change which is readily explicable on the dihydroresorcinol formula (VII) (compare Part II, *loc. cit.*), possible with (VIII), but difficult to reconcile with (IX).

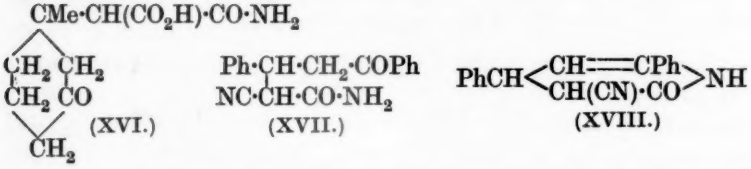

(XI.) (X.) (XII.)

When hydrolysis was interrupted after proceeding for only a few minutes, two substances were obtained—a crystalline, nitrogenous acid (A) and an acidic, nitrogenous gum (B). The latter passed almost entirely into a crystalline, nitrogenous acid (C) on short heating with dilute hydrochloric acid. The two crystalline acids agreed in composition and basicity with the formulæ (X), (XII), (XIII), and (XIV), the last two derivable by an alternative, but less probable fission of (VII) and (VIII). Since neither of the acids gave a colour with ferric chloride, structures (X), (XII), and (XIII) are excluded along with an isomeride (XV) not derivable by fission.


(XIII.) (XIV.) (XV.)

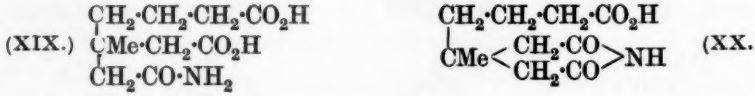
The remaining improbable fission formula (XIV) is an unsuitable representation of either acid. The only alternative formula in

which the *cyclo*hexanone ring is preserved is (XVI), and this, not reasonably derivable from (VII) or (VIII) by fission, adequately represented the properties of the acid (A). It appeared, therefore, that (A) must arise by fission of the dicyclic acid (IX), or some other associated ring compound. Concerning (IX), the production of ketonic tetrahydropyridine rings has been brought about by the action of cyanoacetic ester or cyanoacetamide on open-chain ketones. For example, Kohler and Souther (*J. Amer. Chem. Soc.*, 1922, **44**, 2544, 2907), by the interaction of cyanoacetamide with benzylideneacetophenone, obtained the compound (XVII), which passed on treatment with hydrochloric or hydrobromic acid into a substance represented by them as (XVIII). Whilst this and similar substances are regarded by these authors, contrary to the opinion held by Knoevenagel (*Ber.*, 1903, **36**, 2813), as capable of displaying in full the potential tautomeric capacity expressed by the formula, the occurrence of fission by alkali at a nitrogen–carbon double



bond, as in (XVIII), does not appear to have been observed. Indeed the main features of these substances are their formation and stability in the presence of halogen acids and their capacity for undergoing simultaneous oxidation and reduction to pyridine and piperidine derivatives.

If (IX) correctly represents the structure of the dicyclic compound under consideration, hydrolytic fission at the double bond would lead to reversal of the intramolecular condensation and would account for the production of the acid A (XVI) by the use of alkali. Further fission would be brought about only after further intramolecular condensation, and since caustic alkali is the reagent, the latter would probably be of the Dieckmann type, leading to (VII). This would pass on fission into (X) and (XIX) successively, and finally by prolonged hydrolysis to the open-chain tricarboxylic acid (XI). The intermediate compounds which escape complete



fission and hydrolysis by alkali should then be obtained in the gum B (above). This consisted almost entirely of a substance agreeing

in properties with the formula (XIX); the acid C (above), derived therefrom by short treatment with dilute hydrochloric acid, was the glutarimide (XX). (This imide could not arise from a dicyclic substance of formula VIII.)

It appears certain, therefore, that change from the "meta-" bridged compound (IX) to the "para-" bridged compound (VII) takes place rapidly in alkaline solution. Whilst (IX), however, is extremely stable in acid or neutral solution, the temporary existence of (VII) can only be argued from the nature of its fission products. It is hoped to deal with further factors concerning "meta"-bridging in a subsequent paper.

Experimental.

Condensation of Ethyl Sodiocyanoacetate with 1-*Methyl*-Δ^1-cyclo*hexen*-3-*one*.—The ketone (1 mol.) was added to a cold alcoholic suspension of ethyl sodiocyanoacetate (1 mol.), and the mixture heated for 16 hours on the steam-bath. The cooled product was poured on to ice, acidified with dilute hydrochloric acid, and extracted with ether. The extract was separated into neutral and acidic portions in the usual way.

Ethyl 1-*Methyl*cyclo*hexan*-3-*one*-1-*cyanoacetate* (IV).—The neutral product so obtained yielded on fractionation a small amount of unchanged ketone, but mainly a material, b. p. 160—210°/2 mm. This, on refractionation, gave the pure *ester* as a colourless liquid, b. p. 197°/2 mm. (yield, 21%) (Found: C, 64·3; H, 7·8; N, 6·3. $C_{12}H_{17}O_3N$ requires C, 64·6; H, 7·6; N, 6·3%). The *semicarbazone* crystallised from aqueous alcohol in long needles, m. p. 166° (Found: C, 57·5; H, 7·3. $C_{13}H_{20}O_3N_4$ requires C, 57·4; H, 7·15%).

Methyl 1-*methyl*cyclo*hexan*-3-*one*-1-*cyanoacetate* was prepared in a similar way and obtained, though in poorer yield, as a viscous, colourless liquid, b. p. 185°/2 mm. (Found: C, 63·15; H, 7·3; N, 6·9. $C_{11}H_{15}O_3N$ requires C, 63·15; H, 7·3; N, 6·7%). The *semicarbazone* crystallised from aqueous alcohol in colourless plates, m. p. 183° (Found: C, 53·8; H, 6·7. $C_{12}H_{18}O_3N_4$ requires C, 54·1; H, 6·8%).

1-*Methyl*cyclo*hexenylidene*-3-*cyanoacetic Acid* (V).—The acidic condensation product was a thick red syrup. Occasional scratching over a period of several weeks promoted partial crystallisation and the semi-solid mass was then ground with acetone–petroleum. The brownish crystals were dissolved in acetone and decolorised by boiling with animal charcoal. From the filtered solution the *acid* crystallised in colourless prisms, m. p. 183° with evolution of gas (Found: C, 67·7; H, 6·3; N, 8·1; *M*, 180; equiv., 179. $C_{10}H_{11}O_2N$ requires C, 67·7; H, 6·3; N, 7·9%; *M*, 177). The acid gave no

coloration with ferric chloride and was decomposed on boiling for 1 hour with 10% caustic potash solution into methyl*cyclo*hexenone (semicarbazone, m. p. 199°) and malonic acid.

The methyl ester, obtained from the silver salt and methyl iodide, solidified after distillation (b. p. 165—170°/2 mm.) and crystallised from petroleum in large, flat, colourless prisms (m. p. 60°) which were found by direct comparison to be identical with one form of methyl methyl*cyclo*hexenylidenecyanoacetate (J., 1925, **127**, 2358). Equilibration leading to the mixture of hexenylidene and hexadienyl forms (m. p.'s 74°, 60°, 42°) previously described (*loc. cit.*) was effected with sodium methoxide. The acid which separated from the acidic portion of the condensation product thus represented a single geometrical form.

1-*Methyl*cyclo*hexan*-3-*one*-1-*cyanoacetic acid* was obtained from the corresponding esters by boiling for 2 hours with 10% sodium carbonate solution. Unchanged ester was removed by extraction with ether. By acidification and further extraction, the acid was obtained as a sticky mass which slowly solidified. Recrystallisation from chloroform–petroleum yielded colourless prisms, m. p. 106° (Found: C, 61·3; H, 6·6; N, 7·5. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·6; N, 7·2%).

Propane-$^{1:3}\Pi^{2:4}$-6-*keto*-4-*methyl*-3 : 4 : 5 : 6-*tetrahydropyridine*-5-*carboxylic Acid* (IX).—Methyl*cyclo*hexanonecyanoacetic acid dissolved on boiling with 15% hydrochloric acid, but within 15 minutes a bulky, crystalline mass of the dicyclic compound was precipitated. The same compound was also obtained directly from the monocyclic cyanoacetic ester by boiling with a mixture of equal volumes of hydrochloric acid, water, and alcohol for 1½ hours; large, needle-shaped crystals separated which were freed from traces of unchanged ester by washing with ether. In both cases the yields were almost quantitative. The *acid*, which gave a deep purple colour with ferric chloride, melted at 181° after recrystallisation from ethyl acetate (Found: C, 61·5; H, 6·6; N, 7·5; *M*, cryoscopic in acetic acid, 196; equiv., 197. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·6; N, 7·2%; *M*, 195).

Bromination. Bromine (2 mols.) and the dicyclic acid (1 mol.) in chloroform gave a *bromo*-derivative which crystallised in fine needles, m. p. 186°, and developed no colour with ferric chloride (Found: Br, 45·4. $C_{10}H_{13}O_3NBr_2$ requires Br, 45·2%).

Hydrolytic Fission of the Dicyclic Compound (IX).—(a) *Complete fission.* The dicyclic acid was boiled for 20 hours with 10% caustic potash solution (2 equivs.), ammonia being evolved. By extracting the cooled, acidified solution with ether, an oil was obtained which rapidly solidified (yield, almost quantitative); this, m. p. 125°

after recrystallisation, was identified with β-methylpimelic-β-acetic acid by direct comparison.

(b) *Partial fission.* The acid (10 g.) was boiled for 5 minutes only with 10% caustic potash solution (2 equivs.). The solution was immediately cooled, acidified with dilute hydrochloric acid, and extracted with ethyl acetate. From the extract an acid syrup was obtained which, on slight dilution with acetone and vigorous scratching, partly crystallised. The crystals (acid A) were removed, and the acetone was evaporated from the filtrate; the residue was a syrup (acid B).

1-*Methyl*cyclo*hexan*-3-*one*-1-*malonamic Acid* (XVI).—The acid A, which crystallised in stout prisms (yield, 5·8 g.), m. p. 151° with evolution of carbon dioxide, gave no coloration with ferric chloride. It reverted completely to the dicyclic acid (m. p. 181°) on boiling for 15 minutes with 15% hydrochloric acid. By prolonged hydrolysis with caustic potash, it was converted into β-methylpimelic-β-acetic acid (Found: C, 55·95; H, 7·1; N, 7·0; *M*, monobasic, 212·5. $C_{10}H_{15}O_4N$ requires C, 56·3; H, 7·1; N, 6·6%; *M*, 213).

β-*Methylpimelic Acid* β-*Acetamide* (XIX).—The syrup (acid B) consisted almost entirely of this compound. It still contained a very small amount of the above malonamic acid (acid A), but its constitution follows from its basicity (dibasic), the loss of ammonia on heating it with caustic potash, its conversion into the corresponding imide (below), and the production of β-methylpimelic-β-acetic acid on further hydrolysis with caustic potash.

β-*Methylglutarimide*-β-*butyric Acid* (XX).—When the syrup (acid B) was boiled for 1 hour with 15% hydrochloric acid, a few crystals of the dicyclic acid (IX), formed from the malonamic acid (acid A) which had escaped separation, were deposited. They were removed and the solution was evaporated almost to dryness on a steam-bath. The residue slowly deposited crystals which recrystallised from ethyl acetate in colourless, flat needles, m. p. 139° (yield, 4 g.). This substance gave no coloration with ferric chloride and was unchanged on further boiling with hydrochloric acid. Prolonged boiling with caustic potash caused complete conversion into β-methylpimelic-β-acetic acid. The constitution was confirmed by direct comparison with synthetically prepared β-methylglutarimide-β-butyric acid (Found: C, 56·4; H, 7·1; N, 6·9; *M*, monobasic, 212. $C_{10}H_{15}O_4N$ requires C, 56·3; H, 7·1; N, 6·6%; *M*, 213).

Synthesis of β-*Methylglutarimide*-β-*butyric Acid.*—Dry ammonia was bubbled through the molten anhydride of β-methylpimelic-β-acetic acid (Farmer and Ross, *loc. cit.*) at 135°. When the mass became very viscous and absorbed no more gas, it was cooled, dissolved in water, and boiled for 1 hour with 10% hydrochloric acid;

the imide, which crystallised on cooling, separated from ethyl acetate in long, colourless prisms (Found: C, 56·25; H, 7·1; N, 6·7%; *M*, monobasic, 213); these, alone or mixed with the imide obtained by fission (acid C), melted at 139°.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for grants which have contributed towards the expenses of this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, October 21st*, 1926.]

NOTES.

p-*Dimethylaminobenzylidene Pentaerythritol.* By ARTHUR FAIRBOURNE and JAMES WILLIAM WOODLEY.

IN the course of work on partly substituted polyhydric alcohols (J., 1921, **119**, 1035, 2077; 1925, **127**, 2759) p-*dimethylaminobenzylidene pentaerythritol* was isolated, and its further condensations investigated. The only previously recorded synthesis of a partly substituted pentaerythritol of this type was effected photochemically (Tanasescu, *Bul. Soc. Stiinte Cluj.*, 1923, ii, 111).

Aldehydes usually condense with pentaerythritol to produce the dialkylidene compounds (Read, J., 1912, **101**, 2090), and *p*-dimethylaminobenzaldehyde has itself been recorded as acting in this way (Radulescu and Tanasescu, *Bul. Soc. Stiinte Cluj.*, 1922, i, 192).

On repeating the condensation, however, a different material was obtained when the crude product was crystallised from chloroform, instead of from acetone as recommended. Further investigation showed that the crude product from the Radulescu reaction always contained both mono- and bis-dimethylaminobenzylidene pentaerythritol, whatever strength of sulphuric acid between 10% and 60% was used, the best yield of the bis-compound being obtained with 10% and the best yield (almost quantitative) of the mono with 50%. They could be separated well by fractional crystallisation.

p-Dimethylaminobenzaldehyde and pentaerythritol in equal molecular proportions were thoroughly shaken with warm 50% sulphuric acid and after 12 hours the solution was treated with excess of dilute ammonia. The white precipitate obtained was dried on porous porcelain. Crystallisation from chloroform produced long, white needles of p-*dimethylaminobenzylidene pentaerythritol*, $(CH_2{\cdot}OH)_2C<\begin{matrix}CH_2{\cdot}O\\CH_2{\cdot}O\end{matrix}>CH{\cdot}C_6H_4{\cdot}NMe_2$, m. p. 140° (decomp.),

or very indefinite at about 180° if the specimen had previously been kept at 100° for some hours (Found: C, 62·2; H, 8·2; N, 5·4. $C_{14}H_{21}O_4N$ requires C, 62·9; H, 7·9; N, 5·2%).

In view of this very indefinite melting point, the identity of the substance was confirmed by preparing the methiodide and comparing this with the monomethiodide of bisdimethylaminobenzylidene pentaerythritol and also with that of dimethylaminobenzaldehyde itself, these three methiodides being prepared by heating the respective amines with excess of methyl iodide in sealed tubes for 2 hours at 80—90°, removing the excess of methyl iodide by evaporation from a bath at 70°, and recrystallising the products from alcohol in the case of *p*-dimethylaminobenzylidene pentaerythritol and from ether in the other two cases. The *methiodide* from *p*-dimethylaminobenzylidene pentaerythritol melted and decomposed at 175° (Found: I, 30·8. $C_{15}H_{24}O_4NI$ requires I, 31·0%), that from bis-*p*-dimethylaminobenzylidene pentaerythritol at 220° (Found: I, 22·8. $C_{24}H_{33}O_4N_2I$ requires I, 23·0%), and that from *p*-dimethylaminobenzaldehyde at 160° (Found: I, 43·3. $C_{10}H_{14}ONI$ requires I, 43·6%).

The structure of *p*-dimethylaminobenzylidene pentaerythritol was also established by condensing the compound with a second molecule of *p*-dimethylaminobenzaldehyde and identifying the product with bis-*p*-dimethylaminobenzylidene pentaerythritol by the method of mixed melting point.

Attempts to prepare "mixed" spirans by condensing *p*-dimethylaminobenzylidene pentaerythritol with a molecule of a different aldehyde, *e.g.*, benzaldehyde or cinnamaldehyde, led to the elimination of the *p*-dimethylaminobenzylidene radical and the formation of spirans, $CHR<\begin{matrix}O\cdot CH_2\\O\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}>CHR$, identical (proved by the melting points of mixtures) with those obtained by direct condensation of the respective aldehydes with free pentaerythritol, thus indicating that aldehydic condensations of pentaerythritol are reversible (equilibrium) reactions.

The authors desire to express their indebtedness to the Chemical Society for a grant to one of them (A. F.) which has partly defrayed expenses incurred in this work.—King's College, London, W.C. 2. [*Received, July 15th*, 1926.]

5-Methoxy-α-naphthaldehyde. By John Baldwin Shoesmith and Hannes Rubli.

5-Methoxy-α-naphthaldehyde has been prepared by the catalytic reduction of 5-methoxy-α-naphthoyl chloride as follows: α-Naph-

thylamine-5-sulphonic acid was converted into 1-cyanonaphthalene-5-sulphonic acid by the method of Royle and Schedler (J., 1923, **123**, 1643) and then, by the addition of the calculated quantity of potassium carbonate, into the corresponding potassium salt, which (25 g. in small quantities at a time) was slowly added to a vigorously stirred, fused mixture of 250 g. of sodium hydroxide and 50 g. of water at a temperature which was allowed to rise slowly from 180° to 230° (compare D.R.-P. 413836). The mass, which finally became solid, was cooled and 5-hydroxy-α-naphthoic acid was liberated from an aqueous solution of it by addition of concentrated hydrochloric acid; after recrystallisation from dilute alcohol the acid melted at 235°. The acid (20 g.), dissolved in a solution of 15 g. of potassium hydroxide in 280 c.c. of water, was vigorously stirred with 15 g. of methyl sulphate at 40° for about 1 hour, and the alkaline solution was filtered and acidified. The 5-methoxy-α-naphthoic acid so precipitated was obtained free from the corresponding hydroxy-acid by allowing it to stand in an alkaline solution of diazotised sulphanilic acid for a day, after which the solution was acidified and the precipitate was dried carefully and extracted with dry benzene. The methoxy-acid of m. p. 228° (compare Fuson, *J. Amer. Chem. Soc.*, 1924, **46**, 2787) had to be *quite free* from the hydroxy-acid before conversion into the acid chloride. The acid was dissolved in the calculated quantity of 20% alcoholic potassium hydroxide, and the solution evaporated to dryness. The dried potassium salt (10 g.) was added to a large excess of vigorously stirred thionyl chloride (18 c.c.) in dry benzene (18 c.c.). The whole was finally heated on the water-bath for about 5 minutes, cooled, and filtered from precipitated potassium chloride and acid, and the benzene and thionyl chloride were evaporated under reduced pressure. The residual *5-methoxy-α-naphthoyl chloride* was distilled under reduced pressure. It had b. p. 194°/11 mm., and m. p. 80—81° (Found: Cl, 15·7. $C_{12}H_9OCl$ requires Cl, 16·1%).

5-Methoxy-α-naphthaldehyde.—5-Methoxy-α-naphthoyl chloride (5 g.) in xylene (25 c.c.) in contact with palladinised barium sulphate was reduced by a current of dry hydrogen for 4 hours, the temperature of the bath being 170° (compare Rosenmund, *Ber.*, 1918, **51**, 591). The aldehyde was separated in the usual manner as the bisulphite compound. It crystallised from light petroleum in light yellow plates, m. p. 66° (Found: C, 77·45; H, 5·5. $C_{12}H_{10}O_2$ requires C, 77·45; H, 5·4%). The p-*nitrophenylhydrazone* forms red needles, m. p. 246°, from dilute acetic acid, the *semicarbazone* fine needles, m. p. 246°, from dilute acetic acid, and the *oxime* needles, m. p. 104°, from water or aqueous alcohol.

α-Naphthol, β-naphthol, and their methyl ethers were submitted

to the action of hydrogen in a similar manner, but no change was observed.

The authors wish to acknowledge a grant from the Research Fund of the Chemical Society.—EDINBURGH UNIVERSITY. [*Received, November 12th,* 1926.]

Some New Organo-tin Compounds. By KENNETH KNIGHT LAW.

MANY unsuccessful attempts have been made to improve the yield of tribenzylstannic chloride in the method used by Smith and Kipping (J., 1912, **101**, 2557); with all proportions of magnesium benzyl chloride between $2\frac{3}{4}$ and $3\frac{1}{2}$ mols. the product contains dibenzylstannic chloride, dibenzyl, a small proportion of hexabenzyldistannane and probably also tetrabenzylstannane, although the last-named could not be obtained in a pure state.

Hexabenzyldistannane, $Sn(C_6H_5{\cdot}CH_2)_3{\cdot}Sn(C_6H_5{\cdot}CH_2)_3$, is more conveniently prepared by heating tribenzylstannic chloride with sodium in toluene solution. It crystallises from acetone in colourless tablets, m. p. 147—148°, and is readily soluble in hot acetone or benzene (Found: Sn, 30·3. $C_{42}H_{42}Sn_2$ requires Sn, 30·3%). It is readily decomposed by iodine in benzene solution, giving tribenzylstannic iodide.

Dibenzylethylbutylstannane, $SnEtBu(CH_2Ph)_2$, is prepared by treating dibenzylethylstannic iodide with excess of an ethereal solution of magnesium *n*-butyl bromide and completing the reaction by distilling the ether and heating the residue at about 140° during 1—2 hours. The product, isolated by fractional distillation, is a colourless, highly refractive liquid, b. p. 207—209°/9 mm., 175—180°/3—2·5 mm. (Found: C, 61·4; H, 7·1. $C_{20}H_{28}Sn$ requires C, 61·8; H, 7·2%). It is only moderately easily soluble in ether or acetone but more readily soluble in benzene.

Benzylethyldibutylstannane, $SnEtBu_2{\cdot}CH_2Ph$, was always obtained as a by-product in the above preparation, because the dibenzylethylstannic iodide invariably contained some benzylethylstannic iodide, which could not be removed by fractional distillation. The dibutyl compound is a colourless liquid, b. p. 175—180°/9 mm., 118—122°/2·5—3 mm. (Found: C, 57·4; H, 8·7. $C_{17}H_{30}Sn$ requires C, 57·7; H, 8·6%).

The author wishes to thank Professor Kipping for suggesting this work, and the Salters' Company for a fellowship which enabled him to carry it out.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, November 5th,* 1926.]

OBITUARY NOTICES.

KATHARINE A. BURKE.

DIED JULY 6TH, 1924.

MISS K. A. BURKE came to University College to carry out research work in the laboratory of Sir William Ramsay, having graduated from the Birkbeck College. Under the direction of the writer she investigated the chemical kinetics of the alkyl iodides, the results of which were published in the *Zeitschrift für physikalische Chemie* in the years 1904 and 1909.

For a time Miss Burke acted as a private assistant to Sir William Ramsay, and was engaged on investigations in the field of radioactivity. In 1906 she was appointed a member of the Chemical Staff at University College, and from that time until her death on July 6th, 1924, she continued her teaching work, having charge of the practical laboratory work for students of the Intermediate Science class, and giving courses of lectures to more advanced students on the chemical aspects of radioactive transformations.

Miss Burke was an excellent linguist, and in 1907 made an important contribution to the series of Text-books of Physical Chemistry, edited by Sir William Ramsay, by translating from the Danish an account of the thermochemical researches of Professor Julius Thomsen.

F. G. DONNAN.

JAMES GRANT.

BORN 1858; DIED DECEMBER 7TH, 1925.

JAMES GRANT, who died on December 7th, 1925, at the age of 67, had been a Fellow of the Society since February 6th, 1890.

Born of Scottish parents, he spent his early years in the south, where he entered the teaching profession. Coming to Lancashire, he studied Chemistry at the Owens College under Sir H. E. Roscoe and later became an Associate and Fellow of the Institute of Chemistry. In 1889 he was appointed on the teaching staff of the Manchester Technical School, which subsequently became the College of Technology. He later devoted his attention to foodstuffs and inaugurated and organised the foodstuffs sub-department, keeping in close touch with the related industrial associations. He retired from the staff of the College in March, 1925, after a period of 35 years' service.

Grant was a Master of Technical Science, a Justice of the Peace

for the County of Lancaster, and Chairman of the Chemical section of the Manchester Literary and Philosophical Society.

Among his publications were "Chemistry of Breadmaking," "Confectioners' Raw Materials," "Notes on Costings," and a revised edition of Amos's "Processes of Flour Manufacture," and at the time of his death he was engaged upon a book on the diseases of wheat, bread, and flour.

As a man Grant was punctual, energetic, and thorough in his methods—a successful teacher who communicated his enthusiasm to his students and secured the confidence of those in the industries to which his work applied.

E. L. RHEAD.

WILLIAM JAMES LEWIS.

BORN JANUARY 16TH, 1847; DIED APRIL 16TH, 1926.

PROFESSOR W. J. LEWIS, well known as the Professor of Mineralogy at Cambridge, had been a Fellow of this Society since 1869. He was the second son of the Rev. John Lewis of Llanwyddelan in Montgomeryshire, and was educated at Llanrwst Grammar School and Jesus College, Oxford. Taking first classes in mathematics and natural science, he gained the Senior Mathematical Scholarship and was elected a Fellow of Oriel College in 1872. This fellowship he held until his death. For a short time he was an assistant master at Cheltenham College and an assistant in the Mineralogical Department of the British Museum (1875—77), and he took part in two solar eclipse expeditions. In 1879 he acted as deputy to Prof. W. H. Miller at Cambridge, and in 1881 he succeeded Miller as Professor of Mineralogy. Like Whewell and Miller before him, he was more interested in the crystallographic side of mineralogy, and the subject as taught had as much bearing on chemistry, physics, and petrology as on mineralogy—he might, indeed, have been called Professor of Crystallography. Under his *régime* the department and the collection of minerals were very considerably increased, and many more students took mineralogy as a subject for an honours degree. In 1925 and 1926 there were respectively 46 and 43 Tripos candidates in this subject. All these students must at least have been impressed with the importance of the crystalline structure of matter, apart from chemical composition and the mass physical properties.

Lewis's first scientific papers appeared in the *Journal* of this Society in 1875. These dealt with the crystallography of mairogallol and leucaurin; and his later papers were on the crystallography of various minerals, many of which he collected himself

in Switzerland. His "Treatise on Crystallography" (1899) is still the best text-book on geometrical crystallography. He was elected a Fellow of the Royal Society in 1909. L. J. S.

SHIGETAKE SUGIURA.

BORN MARCH 3RD, 1855; DIED FEBRUARY 13TH, 1924.

THE life of Shigetake Sugiura was, in certain respects, a remarkable one. Beginning with a promising scientific career, he was destined soon to renounce the study of science because of illness, and yet, fighting always with his delicate health, he was able to make himself known and respected throughout Japan as one of her ablest thinkers and most gifted teachers.

Shigetake, second son of Shigebumi Sugiura, was born on March 3rd, 1855, in the small town of Zeze, not far from Kyōtō. Receiving a general education in his native town, young Sugiura soon distinguished himself by his unusual ability and firmness of character, and when, soon after the Restoration, the Central Government asked every clan (according to its size) to send either one, two, or three of its most promising young students to Tokyo to be educated in Western science, he was selected by the Feudal Lord of Zeze to be the "contribution student" of his clan. This was in 1870, when Sugiura was fifteen years of age.

The Government school, which Sugiura entered and in which English and the elements of Western sciences were taught, was known as Daigaku Nanko, an institution which has since grown into the present Imperial University of Tokyo. When, in 1874, special courses of study were first established, he took up Chemistry as his future profession. R. W. Atkinson was then Professor of Chemistry, and for two years Sugiura worked diligently under him. About this time, promising students were being selected by the Government to be sent abroad for further study, and together with some others, of whom the writer was one, Sugiura was in June, 1876, elected to a Foreign Scholarship and sent to England to continue his study of Chemistry.

With the idea of studying Agricultural Chemistry, Sugiura entered the Agricultural College in Cirencester in October, 1876, but finding that the agricultural conditions in England were totally different from those prevailing in Japan, he soon left Cirencester and went to Manchester, entering Owens College in December of the same year. Here he was brought into close personal contact with Roscoe and Schorlemmer, of both of whom Sugiura, in his after years, never ceased to speak in terms of affection and reverence.

In Manchester, he was also constantly associated with H. B. Baker, C. F. Cross, and Pattison Muir, and the few papers he published while in Owens College were in collaboration with one or other of these men. In 1878 he was elected a Fellow of the Chemical Society and became a life-member.

In the same year, he moved to London and entered the Royal College of Chemistry in South Kensington, where Frankland was then Professor of Chemistry. During the course of a conversation with the writer in London in December, 1901, Sir Henry Roscoe told him the following story in reference to this incident in Sugiura's life: Sugiura carried off the first prize in his first year's examination at Owens College, but at the end of the second year he was placed second on the list; soon afterwards, Sir Henry learnt that Sugiura was leaving the college and found that he considered himself disgraced by not having taken the first place. This story is repeated in "The Life and Experience of Sir Henry Enfield Roscoe" (London, 1906, p. 114), written by himself. It appears, however, that the story arose from a misunderstanding on the part of Sir Henry, as Sugiura himself told the writer afterwards, and that his only motive in leaving Owens College and entering the Royal College of Chemistry was his desire to widen his experience by working in another laboratory under another great chemist such as Frankland. Indeed, at one time, Sugiura even thought of going to Germany.

Whatever may have been the real motive of his leaving Owens College, Sugiura was soon destined to give up his study of chemistry altogether, for in the following year his health was so much impaired, mainly from neurasthenia, that the doctor advised him to take a holiday and go to the seaside. Following this advice, he went to Hastings, but without any beneficial results, and, after much worry and anxiety, he at last returned to Japan in May, 1880.

Although somewhat improved after the return to Japan, Sugiura's health was still in a more or less indifferent condition, and it was, therefore, rather wonderful that, at one time or another, he was able to assume such responsible duties as those of the director of a Preparatory School attached to the University of Tokyo (1882—85), member of the Lower House of the Imperial Diet (1890), and member of the Higher Education Council (1897—98), besides several other duties of a more personal nature. For some years after returning from England he was also a constant contributor to magazines and daily papers, writing on educational, ethical, philosophical, political, and other questions, and expounding more particularly what he called a Scientific Religion, which was an attempt at formulating a moral code based upon modern science. This was an idea Sugiura nourished while still in England.

Sugiura again suffered from neurasthenia in 1899, and, although his recovery was then comparatively speedy, within a few years he suffered from the same complaint for the third time, to lie in bed continuously for seven long years (1902—1909). All hope of his recovery was given up, and yet, miraculously, although slowly, he once more recovered his health, and, what is even more remarkable, he got better than he had ever been, whilst his mental activity never showed even the slightest sign of deterioration.

Indeed, Sugiura's most important work began a few years after his recovery from his third and most serious illness, for in 1914 he was called to the responsible duties of a tutor to H.I.H. The Crown Prince and, later, also to H.I.H. Princess Nagako, who was then betrothed to the Crown Prince. Ethics was the subject Sugiura taught his Imperial pupils, and with his profound knowledge of both Eastern and Western cultures, combined with his noble and unselfish personality, he was undoubtedly the man most fitted for the important duties of a tutor to the future Sovereign and his future Consort. In this capacity, Sugiura served most meritoriously for seven years, and this was destined to be the last of the public services he rendered to his country.

Towards the end of 1923, Sugiura's health began to decline rapidly, and on February 13th, 1924, he passed away peacefully at the age of 69, leaving a widow and five children.

List of Chemical Papers published by Sugiura.

1. "On a Slight Modification of Hofmann's Vapour-density Apparatus" (with M. M. Pattison Muir). J., 1877, **32**, 140—144.

2. "On Essential Oil of Sage" (with M. M. Pattison Muir). J., 1878, **33**, 292—298.

3. "Action of the Halogens at High Temperatures upon Metallic Oxides" (with C. F. Cross). J., 1878, **33**, 405—409.

4. "On the Decomposition of Ultramarine by Carbonic Acid." *Chem. News*, 1878, **37**, 213.

5. "On the Formation of Barium Periodate" (with C. F. Cross). J., 1879, **35**, 118—119.

6. "Note on the Magnesium Vanadates" (with H. B. Baker). J., 1879, **35**, 713—716.

JOJI SAKURAI.

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OF

THE CHEMICAL SOCIETY

SUPPLEMENTARY NUMBER,

CONTAINING

TITLE-PAGES, CONTENTS,

AND

INDEXES.

1926.

LONDON:
GURNEY AND JACKSON
33, PATERNOSTER ROW, E.C. 4.

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INDEX OF AUTHORS' NAMES, 1926.

A.

Aeschlimann, *John A.*, the relative stability of the quinolone and indolinone rings, 2902.

Aitken, (*Miss*) *Margaret F.*, and *Thomas H.* **Reade**, action of nitrous acid on *p*-iododimethylaniline, 1896.

Allan, *James*, *Albert E.* **Oxford**, *Robert* **Robinson**, and *John C.* **Smith**, the relative directive powers of groups of the forms RO and RR′N in aromatic substitution. Part IV. A discussion of the observations recorded in Parts I., II., and III., 401.

Allan, *James*, and *Robert* **Robinson**, the relative directive powers of groups of the forms RO and RR′N in aromatic substitution. Part I., 376.

a new synthesis of fisetin and of quercetin, 2334.

Allmand, *Arthur J.*, and *Lewis* **Reeve**, the photochemical decomposition of aqueous oxalic acid solutions, 2834.

the photochemical decomposition of aqueous formic acid solutions, 2852.

Allpress, *Charles F.*, the transformation of monomethyl fructose into derivatives of γ-fructose, 1720.

Applebey, *Malcolm P.*, and *John A.* **Lanyon**, the oxidation of ammonium sulphide, 2983.

Ashley, *Julius N.*, derivatives of stilbene, 2804.

Ashworth, *Frank.* See *George N.* **Burkhardt**.

Atkinson, *Harold*, and *Isidor M.* **Heilbron**, styrylpyrylium salts. Part VI. Styryl derivatives of 9-methylxanthylium chloride and 3:6-dihydroxy-9-methylxanthylium chloride, 676.

preparation of hydroxybenzophenones and hydroxyxanthones, 2688.

Aufenast, *Frederick*, and *Henry* **Terrey**, the existence of the suboxides of lead and thallium, 1546.

Austin, *Harold E.* See *Stephen H.* **Piper**.

Ayyar, *Panchandana R.* See *Darab D.* **Kanga**.

B.

Bailey, *Kenneth C.* See *Emil A.* **Werner**.

Baird, *William*, and *Forsyth J.* **Wilson**, the action of hydrazines on semicarbazones. Part II., 2367.

Baker, *Herbert B.* See *Harry L.* **Riley**.

Baker, *John W.*, the chemistry of polycyclic structures in relation to their homocyclic unsaturated isomerides. Part VI. Some reactions of *iso*phorone, 663.

Baker, *John W.*, and *Christopher K.* **Ingold**, the nature of the alternating effect in carbon chains. Part IX. The directive influence of groups of the form –CRR′·NO_2 in aromatic substitution, 2462.

Baker, *Wilson*, synthesis of 7-methoxy-3-(6′-bromohomopiperonyl)-2-methyl-1:4-benzopyrone, 1074.

Baker, *Wilson*, and *Robert* **Robinson**, synthetical experiments in the *iso*flavone group. Part II. A synthesis of methylgenistein (methylprunetol) dimethyl ether and the constitution of prunetol (genistein), 2713.

Balaban, *Isidore E.*, the action of alkaline arsenites on some halogenated organic compounds, 569.

Banfield, *Francis H.*, and *Joseph* **Kenyon**, the constitution of the condensation product of β-phenylhydroxylamine and acetone, 1612.

Barcroft, *Joseph*, hæmoglobin, 1146.

Beard, *Herbert G.* See *Herbert H.* **Hodgson**.

Bell, *Frank*, and *Joseph* **Kenyon**, acetyl-*o*-phenylenediamine and acetyl-1:2:3-benztriazole, 954.

the hydrolysis of acetyl-*o*-benzylideneaminophenol, 1893.

investigations in the diphenyl series. Part II. Substitution reactions, 2705.

investigations in the diphenyl series. Part III. Derivatives of 4-hydroxydiphenyl, 3044.

Bell, *Frank*, *Joseph* **Kenyon**, and *Percy H.* **Robinson**, investigations in the diphenyl series. Part I. Migration reactions, 1239.

Bell, *James*, the hydrolysis of guanidine, 1213.

Belton, *Joseph W.*, *Robert O.* **Griffith**, and *Andrew* **McKeown**, the thermal reactivity of ozone in presence of hydrogen, 3153.

Birch, *Stanley F.*, and *Woodford S. G. P.* **Norris**, the chemistry of petroleum. Part III. The acid sludge from the refining of Persian kerosene. Part I. The aromatic hydrocarbons, 2545.

Bishop, *Gerald*, and *Oscar L.* **Brady**, the oximes of 2:4-dinitrobenzil and the Beckmann change, 810.

Black, *Ian M. A.* See (*Sir*) *James C.* **Irvine**.

Blakey, *William*, *Hamilton* **McCombie**, and *Harold A.* **Scarborough**, the velocity of saponification of mono- and di-substituted chloro- and methoxy-derivatives of ethyl benzoate, 2863.

Bonnell, *David G. R.*, and *William J.* **Jones**, the equilibrium between ethyl alcohol and the alkali and alkaline-earth salts. Part I., 318.

the dissociation pressures of alcoholates. Part I., 321.

Bowen, *Edmund J.*, and *Harold G.* **Watts**, the photolysis of acetaldehyde and of acetone, 1607.

Boyd, *David R.*, and *Frederick J.* **Smith**, the formation of phosphinic acids from triarylmethoxyphosphorus dichlorides, 2323.

Bradley, *Albert J.* See *Heinz* **Müller**.

Bradley, *William*, and *Robert* **Robinson**, the hydrolytic fission of some substituted dibenzoylmethanes, 2356.

Brady, *Oscar L.*, and *Frederick P.* **Dunn**, the isomerism of the oximes. Part XXVIII. The Beckmann rearrangement of the *N*-methyl ethers of aldoximes, 2411.

Brady, *Oscar L.*, *Frederick P.* **Dunn**, and *Richard F.* **Goldstein**, the isomerism of the oximes. Part XXVI. The methyl ethers of the aldoximes, 2386.

Brady, *Oscar L.*, and *Richard F.* **Goldstein**, the isomerism of the oximes. Part XXV. The dissociation constants of some isomeric aldoximes, 1918.

the isomerism of the oximes. Part XXVII. The mechanism of methylation of the aldoximes, 2403.

Brady, *Oscar L.* See also *Gerald* **Bishop**.

Briers, *Frank*, *David L.* **Chapman**, and *Ernest* **Walters**, the influence of the intensity of illumination on the velocity of photochemical changes; the determination of the mean life of a hypothetical catalyst, 562.

Briscoe, *Henry V. A.*, *Percy L.* **Robinson**, and *George E.* **Stephenson**, the density of boric oxide glass and the suspected variation in the atomic weight of boron, 70.

density of boric oxide from a fractional crystallisation of boric acid, 954.

Briscoe, *Henry V. A.* See also *John* **Cleminson**, *Victor G.* **Jolly**, *Percy L.* **Robinson**, and *Leonard A.* **Sayce**.

Britton, *Hubert T. S.*, hydrogen electrode studies of the precipitation of basic chromates, borates, and carbonates, 125.

hydrogen electrode studies of the reactions between solutions of salts of weak metallic bases and the acetate, oxalate, and tartrate of sodium, with a note on the effect of dextrose on zirconium chloride solution, 269.

the basic sulphate of copper, 2868.

Brooker, *Leslie G. S.*, and *Samuel* **Smiles**, a method of inserting the thioaryl group, 1723.

Buchanan, *John Y.*, obituary notice of, 993.

Burke, (*Miss*) *Katharine A.*, obituary notice of, 3244.

Burkhardt, *George N.*, and *Arthur* **Lapworth** [with *Frank* **Ashworth**], arylsulphuric acids, 684.

Burns, *Alan C.* See *Frederick M.* **Rowe**.

Burrage, *Leslie J.*, studies of equilibria in systems of the type lead halide–potassium halide–water, 1703.

the solubility of lead iodide in solutions of sodium chloride at 25°, 1896.

Burstall, *Francis H.* See *Gilbert T.* **Morgan**.

Burton, *Harold*, and *Charles S.* **Gibson**, 10-chloro-5:10-dihydrophenarsazine and its derivatives. Part I. The synthesis, preparation, and some properties of 10-chloro-5:10-dihydrophenarsazine, 450.

10-chloro-5:10-dihydrophenarsazine and its derivatives. Part II. The action of primary chloroarsines on diphenylamine and its homologues, 464.

10-chloro-5:10-dihydrophenarsazine and its derivatives. Part III. Homologues and amino-, chloro-, and cacodyl derivatives, 2241.

Burton, *Harold*, *Frederick* **Hammond**, and *James* **Kenner**, mercuration of *o*-nitrotoluene, 1802.

Bury, *Frank W.* See *Elwyn* **Roberts**.

Butler, *John A. V.*, and *Eavard S.* **Hiscocks**, the solubilities of thallous chloride in salt solutions at 0°, 25°, and 50°, and its heats of solution, 2554.

Butler, *John A. V.* See also *Sydney R.* **Carter.**

C.

Cahn, *Robert S.*, degradative experiments in the morphine group, 2562.

Cahn, *Robert S.*, and *Robert* **Robinson**, the morphine group. Part IV. A new oxidation product of codeine, 908.

Campbell, *Alan N.*, the conductivity of phosphoric acid solutions at 0°, 3021.

Campbell, *Colin*, and *Donald W.* **Woodhead**, the ignition of gases by an explosion-wave. Part I. Carbon monoxide and hydrogen mixtures, 3010.

Campbell, *Ray*, *Robert D.* **Haworth**, and *William H.* **Perkin**, *jun.*, synthetical experiments in the *iso*quinoline group. Part VI. A synthesis of derivatives of paraberine, 32.

Capper, *Norman S.*, and *Joseph K.* **Marsh**, absorption spectra of condensed nuclear hydrocarbons, 721.

Carter, *John S.* See *Harry M.* **Dawson.**

Carter, *Sydney R.*, *John A. V.* **Butler**, and *Frank* **James**, the oxidation potential of the system selenium dioxide–selenium, 930.

Carter, *Sydney R.*, and *Norman H.* **Hartshorne**, the system ferrous oxide–phosphoric acid–water and some of its oxidation products, 363.

Carter, *Sydney R.*, and *Frederick M.* **Lea**, observations on liquid boundaries and diffusion potentials, 834.

Carter, *Sydney R.* See also *Gilbert T.* **Morgan.**

Caspari, *William A.*, the crystal structure of catechol, 573.

the crystal structure of quinol. Part I., 2944.

Caven, *Robert M.*, and *William* **Johnston**, equilibrium in the systems nickel sulphate–potassium sulphate–water, zinc sulphate–potassium sulphate–water, and manganese sulphate–potassium sulphate–water at 25°, 2623.

Challenger, *Frederick*, *Arnold T.* **Peters**, and *Jacob* **Halévy**, the introduction of the selenocyano-group into aromatic compounds, 1648.

Chamberlain, *Norman H.*, *John* **Hume**, and *Bryan* **Topley**, the hydrates of manganous oxalate, 2620.

Chapman, *A. Chaston*, and *H. J.* **Plenderleith**, examination of an ancient Egyptian (Tut-ankh-Amen) cosmetic, 2614.

Chapman, *Arthur W.*, imino-aryl ethers. Part IV. Reversible migration of an aryl group, 2296.

Chapman, *David L.*, *Richard A.* **Goodman**, and *Rodney T.* **Shepherd**, the direct synthesis of nitrous oxide, 1404.

Chapman, *David L.* See also *Frank* **Briers.**

Chapman, *William R.*, and *Richard V.* **Wheeler**, the propagation of flame in mixtures of methane and air. Part IV. The effect of restrictions in the path of the flame, 2139.

Charlton, *William*, *Walter N.* **Haworth**, and *Stanley* **Peat**, a revision of the structural formula of glucose, 89.

Chattaway, *Frederick D.*, the condensation of phenols with chloral, 2720.

Chattaway, *Frederick D.*, and *Edward A.* **Coulson**, the nitration of benzil, 1070.

Chattaway, *Frederick D.*, and *William R. C.* **Curjel**, the crystalline forms of 5-nitrosalicylic acid and of related compounds, 3210.

Chattaway, *Frederick D.*, and *George D.* **Parkes**, substituted dihydropentazines; a new series of cyclic nitrogen compounds, 113.

Child, *Reginald*, and *Samuel* **Smiles**, synthesis of naphthathioxins, 957.

photoTropic amino-aryl disulphoxides, 2696.

Chirnoaga, *Eugen*, the catalytic decomposition of solutions of sodium hypochlorite by finely divided metallic oxides, 1693.

Christiansen, *Jens A.*, the equilibrium between methyl formate and methyl alcohol, and some related equilibria, 413.

Christie, *George H.*, *Albert* **Holderness**, and *James* **Kenner**, the molecular configurations of polynuclear aromatic compounds. Part VI. *β*-Dinitrodiphenic acid; its constitution and resolution into optically active components, 671.

Christie, *George H.*, and *James* **Kenner**, the molecular configurations of polynuclear aromatic compounds. Part V. The identity of the nitration products derived from 2:7- and 4:5-dinitrophenanthraquinones, 470.

Ciamician, *Giacomo L.*, obituary notice of, 996.

Claassen, *Antony.* See *Andreas* **Smits.**

Clark, *Leslie M.*, the quaternary salts of benzoxazoles, 232.

Clark, *Walter*, the electrometric titration of halides, 749.

Cleminson, *John*, and *Henry V. A.* **Briscoe**, the catalytic dissociation of carbon monoxide, 2148.

Clough, *George W.*, the relationship between the optical rotatory powers and the relative configurations of optically active compounds. Part III., 1674.

Coffey, *Samuel*, the mercuration of aromatic substances. Part II. *o*-Nitrotoluene, 637.

the mercuration of aromatic substances. Part III. *p*- and *m*-Nitrotoluenes, 3215.

Collar, (*Miss*) *Winifred M.*, and *Sydney G. P.* **Plant**, derivatives of tetrahydrocarbazole. Part V. Carboxylic acids, 808.

Cook, (*Miss*) *Alison M. R.* See *John* **Read**.

Cook, *James W.*, the reactivity of *meso*-substituted anthracenes. Parts I., II., and III., 1282, 1677, 2160.

Cooper, *Conrad J. A.*, *Walter N.* **Haworth**, and *Stanley* **Peat**, the constitution of the disaccharides. Part X. Maltose, 876.

Cooper, *Kenneth E.*, *Christopher K.* **Ingold**, and (*Mrs.*) *Edith H.* **Ingold**, the correlation of additive reactions with tautomeric change. Part V. The structural conditions affecting mobility and equilibrium in additive reactions. 1868.

Cooper, *Kenneth E.*, and (*Mrs.*) *Edith H.* **Ingold**, the reversibility of triazan formation, 1894.

Coops, *Jan.* See *Pieter E.* **Verkade**.

Corbet, *Alexander S.*, a phase-rule study of the zinci-, cadmi-, mercuri-, and nickelo-cyanides of potassium, 3190.

Coulson, *Edward A.* See *Frederick D.* **Chattaway**.

Coutie, *Alexander*, termolecular reactions; reduction of silver acetate by sodium formate, 887.

Coward, *Hubert F.*, and *Francis J.* **Hartwell**, extinction of methane flames by diluent gases, 1522.

Cranston, *John A.*, and *Alexander Y.* **Livingstone**, a comparison of some of the physical properties of the alkali cyanates and azides, 501.

Crossley, *Arthur W.*, presidential address, 978.

Cruickshank, *James.* See *Alexander* **Findlay**.

Cumming, *William M.*, and *William* **Good**, the estimation of ferro- and ferri-cyanides, 1924.

Curjel, *William R. C.* See *Frederick D.* **Chattaway**.

D.

Davies, *John S. H.* See *Frederick M.* **Rowe**.

Davies, *Samuel H.*, obituary notice of, 1004.

Davies, *William*, and *Geoffrey W.* **Leeper**, a study of the rule of the conservation of the type of substitution in aromatic substances. Part I. Chlorination of 2-chloro-4-nitrotoluene, 1413.

Dawson, *Harry M.*, and *John S.* **Carter**, acid and salt effects in catalysed reactions. Part I., 2282.

Dawson, *Harry M.*, and *Norman C.* **Dean**, acid and salt effects in catalysed reactions. Part II. The minimum reaction velocities for acid–salt mixtures, 2872.

Dawson, *Harry M.*, and *Charles R.* **Hoskins**, acid and salt effects in catalysed reactions. Part III. Dependence of the characteristics of the minimum-velocity mixture on the concentration of the acid and the application of minimum velocity to the determination of catalytic and ionisation constants, 3166.

Dawson, *Harry M.* See also *Alan E.* **Wadsworth**.

Dean, *Norman C.* See *Harry M.* **Dawson**.

Deering, *William H.*, obituary notice of, 1006.

Denham, *Henry G.*, and *John* **Packer**, an improved hydrogen sulphide generator, 1344.

Dennett, *Henry G.*, and *Eustace E.* **Turner**, orientation effects in the diphenyl series. Part I., 476.

Dennler, *Walter S.* See *Alexander* **McKenzie**.

Dickinson, *Robert*, the condensation of benzyl methyl ketone with salicylaldehyde, 2234.

Dimond, *Denys W.* See *Samuel* **Glasstone**.

Dolid, *Jacob.* See *George S.* **Whitby**.

Domleo, *Allan*, and *Joseph* **Kenyon**, investigations on the dependence of rotatory power on chemical constitution. Part XXX. The resolution of methyl*cyclo*hexylcarbinol, 1841.

Drew, *Harry D. K.*, cyclic organometallic compounds. Part I. Compounds of tellurium, 223.

cyclic organo-metallic compounds. Part II. Tellurylium compounds, a new series of intensely coloured tellurium derivatives; the migration of anions in solids, 3054.

Drew, *Harry D. K.*, and *Walter N.* **Haworth**, a critical study of ring structure in the sugar group, 2303.

Drumm, *Peter J.* See *Joseph* **Reilly**.

Drummond, *Allan M.*, and *David T.* **Gibson**, co-ordinated mercaptides, 3073.

Drummond, *Allan M.*, and *Andrew* **McMillan**, the oxidation of narcotine by hydrogen peroxide, 2702.

Duin, *Constant F. van*, *Robert* **Robinson**, and *John C.* **Smith**, the morphine group. Part III. The constitution of neopine, 903.

Dunn, *Frederick P.* See *Oscar L.* **Brady**.

Dunn, *John S.*, the diffusion of zinc in the α-series of solid solution in copper, 2973.

Dunnicliff, *Horace B.*, and *Sukh D.* **Nijhawan**, the action of hydrogen sulphide on a neutral solution of potassium permanganate, 1.

Dunnicliff, *Horace B.* See also *M. Abdul* **Hamid**.

Dutt, *Sikhibhushan*, ring-chain tautomerism. Part XV. The phenolsuccineins and -glutareins, 1132.

a theory of colour on the basis of molecular strain; the effect of chromophoric superposition, 1171.

Dyson, *George M.*, *Herbert J.* **George**, and *Robert F.* **Hunter**, the interaction of thiocarbonyl chloride and chlorosubstituted anilines and the inhibitory action of *o*-substituents, 3041.

Dyson, *George M.*, *Robert F.* **Hunter**, and *Charles* **Soyka**, aminobenzthiazoles. Part VII. The 2-alkylamino-β-naphthathiazole system, 2964.

E.

Earl, *John C.*, and *John* **Read**, piperitone. Part VIII. The condensation of piperitone with aldehydes, 2072.

Edwards, *George A.*, synthetical work on the *iso*quinoline alkaloids. Part I. Substituted *o*-carboxyphenylethylamines, 740.

synthetical work on the *iso*quinoline alkaloids. Part II. A method of opening the rings of cyclic ketones, 813.

Elford, *William J.* See *James W.* **McBain**.

Elliott, *George A.*, *Leslie L.* **Kleist**, *Frederick J.* **Wilkins**, and *Harry W.* **Webb**, nitrosylsulphuric acid. Part I., 1219.

Emeléus, *Harry J.*, the inhibition of the glow of phosphorus, 1336.

Emeléus, *Harry J.*, the spectra of the phosphorescent flames of carbon disulphide and ether, 2948.

Evans, *Derek C.* See *Alexander S.* **Russell**.

Ewart, *Frederick K.*, and *Humphrey R.* **Raikes**, the viscosities and densities of anhydrous methyl alcohol and of solutions of some halides of sodium and potassium in this solvent, 1907.

Ewart, *Frederick K.* See also *Humphrey R.* **Raikes**.

Ewbank, (*Miss*) *Elinor K.* See *Thomas W. J.* **Taylor**.

F.

Fairbourne, *Arthur*, and *Graham E.* **Foster**, the partial esterification of polyhydric alcohols. Part IV. The oxidation of allyl esters to α-monoglycerides, 3146.

the partial esterification of polyhydric alcohols. Part V. The α-structure of alleged β-monoglycerides, 3148.

Fairbourne, *Arthur*, and *James W.* **Woodley**, *p*-dimethylaminobenzylidene pentaerythritol, 3240.

Fairweather, *David A.*, and *Oswald J.* **Walker**, the mechanism of Kolbe's electrosynthesis, 3111.

Farmer, *Ernest H.*, and *Jacob* **Kracovski**, the electrolytic synthesis of tetramethyladipic acids, 2318.

Farmer, *Ernest H.*, and *Henry L.* **Richardson**, the chemistry of the glutaconic acids. Part XX. Tetrahydro*iso*phthalic acid, 2172.

Farmer, *Ernest H.*, and *John* **Ross**, properties of conjugated compounds. Part I. Conjugative associations in extended "conjugated" systems, 1570.

the formation and stability of associated alicyclic systems. Part III. The change from "meta" to "para" bridged rings, 3233.

Farmer, *Walter*, and *James B.* **Firth**, production of arsenic subsulphide; reduction of certain arsenic compounds by sodium hyposulphite [hydrosulphite], 119.

Farrow, *Maurice D.*, and *George A. R.* **Kon**, the chemistry of the three-carbon system. Part VI. Some systems containing the benzoyl group, 2128.

Farrow, (*Miss*) *Monica*, the solubilities of sodium, potassium, and calcium ferrocyanides. Part I., 49.

Faulkner, *Irvine J.*, and *Thomas M.* **Lowry**, studies of dynamic isomerism. Part XXII. Methyl alcohol as an amphoteric solvent for the mutarotation of the sugars, 1938.

Fear, (*Miss*) *Christina M.*, and *Robert C.* **Menzies**, applications of thallium compounds in organic chemistry. Part III. Alkylations, 937.

Finch, *George I.*, and *Reginald P.* **Fraser**, purification of phosphoric oxide, 117.

Findlay, *Alexander*, and *James* **Cruickshank**, the reciprocal salt pair (Na, Ba)-(Cl, NO_3) in aqueous solution at 20°, 316.

Finlayson, *Hedley H.*, examination of the volatile oils from *Xanthorrhœa arborea*, *X. hastilis*, and *X. reflexa*, 2763.

Firth, *James B.* See *Walter* **Farmer**.

Flürscheim, *Bernhard*, and *Eric L.* **Holmes**, the laws of aromatic substitution. Part V. The directing effect of electrolytically dissociated groups, 1562.

Fodor, *Andor*, and *Rassa* **Riwlin**, studies in adsorption by an optical method; fixation by dispersoids of methylene-blue within the disperse phase, 102.

Forster, *Martin O.*, and *Keshaviah A. N.* **Rao**, isomeric phenylserines, 1943.

studies in the camphane series. Part XLI. The unstable modification of *iso*nitrosocamphor, 2670.

Forsyth, *Robert*, *Vishvanath K.* **Nimkar**, and *Frank L.* **Pyman**, the nitration of benzamidines, 800.

Forsyth, *Robert*, and *Frank L.* **Pyman**, the tautomerism of amidines. Part VI. Methylation of 4-anilino-2-phenyl-6-methylpyrimidine, 2502.

nitration of 2-, 3-, and 4-phenylpyridines, 2912.

Foster, *Graham E.* See *Arthur* **Fairbourne**.

Fowles, *George*, a study of the basic copper sulphates, 1845.

Francis, *Francis*, and *Harry F.* **Gauntlett**, the non-acidic oxidation products of paraffin wax, 2377.

Francis, *Francis*, and *Norman E.* **Wood**, the boiling points of some higher aliphatic *n*-hydrocarbons, 1420.

Francis, *Wilfrid*, and *Richard V.* **Wheeler**, resins in coal; studies in the composition of coal, 1410.

Fraser, *Reginald P.* See *George I.* **Finch**.

Fulton, *James D.*, action of acetylene tetrabromide on organic bases, 197.

Fulton, *James D.* See also *Thomas S.* **Patterson**.

G.

Gait, *Alban J.* See *Ernest W.* **McClelland**.

Gane, *Richard*, and *Christopher K.* **Ingold**, the influence of carbon rings on the velocity of reactions involving their side chains. Part I. The hydrolysis of cyclic and open-chain malonic esters, 10.

Ganguly, *Phani B.*, experiments on the formation of mother-of-pearl, 1381.

Gardiner, *James H.*, the ultra-violet spectra of praseodymium, neodymium, samarium, europium, and erbium, 1518.

Garner, *William E.*, *F. C.* **Madden**, and *J. E.* **Rushbrooke**, alternation in the heats of crystallisation of the normal monobasic fatty acids. Part II., 2491.

Garran, *Richard R.*, the ternary system sodium thiosulphate–sodium sulphate–water, 848.

Gatewood, (*Miss*) *Elisabeth S.*, and *Robert* **Robinson**, a synthesis of pyrylium salts of anthocyanidin type. Part X. Delphinidin chloride 3-methyl ether, 1959.

Gatterer, *Alois*, the absorption of gases by colloidal solutions, 299.

Gauntlett, *Harry F.* See *Francis* **Francis**.

George, *Herbert J.* See *George M.* **Dyson**.

Ghosh, *Bhupendranath*, parallelism between the effect of neutral salts on the electrical charge of hydrated manganese oxides and the concentration of hydrogen ions liberated, 2605.

Ghosh, *Bivas C.* See *Jnanendra N.* **Mukherjee**.

Ghosh, *Gajendra N.* See *Jnanendra N.* **Mukherjee**.

Gibson, *Charles S.*, *Kalvoi V.* **Hariharan**, *Kottiagath N.* **Menon**, and *John L.* **Simonsen**, derivatives of naphthaquinolines and naphthaisoquinolines, 2247.

Gibson, *Charles S.* See also *Harold* **Burton**.

Gibson, *David T.*, *John M.* **Robertson**, and *James* **Sword**, the oxidation of certain sesquiterpenes with chromyl chloride and chromic acid, 164.

Gibson, *David T.* See also *Allan M.* **Drummond**.

Gibson, *George P.*, the monochloro-derivatives of *m*-cresol, 1424.

Glasstone, *Samuel*, studies of electrolytic polarisation. Part IV. The electro-deposition potentials of iron, cobalt, and nickel, 2887.
studies of electrolytic polarisation. Part V. The electro-deposition potentials of alloys of iron, cobalt, and nickel, 2897.
Glasstone, *Samuel*, *Denys W.* **Dimond**, and *Edgar R.* **Harris**, solubility influences. Part III. The salting-out effect of mixtures on aqueous solutions of ethyl acetate, 2939.
Glasstone, *Samuel*, *Denys W.* **Dimond**, and *Edward C.* **Jones**, solubility influences. Part II. The effect of various salts on the solubility of ethyl acetate in water, 2935.
Goldstein, *Richard F.* See *Oscar L.* **Brady**.
Goldsworthy, *Leonard J.*, the reactivity of alkyl iodides with sodium benzyl oxide, 1102.
the velocities of the reactions between ethyl iodide and the sodium salts of various substituted phenols in ethyl-alcoholic solution, 1254.
Good, *William*. See *William M.* **Cumming**.
Goodman, *Richard A.* See *David L.* **Chapman**.
Gornall, *Frank H.*, and *Robert* **Robinson**, 2:3:4-trinitrotoluene, 1981.
Gorowara, *Faqir C.* See *Herbert H.* **Hodgson**.
Goss, *Frank R.*, and *Christopher K.* **Ingold**, the conditions underlying the formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. Part IX. Products derived from suberic and azelaic acids, 1471.
Goss, *Frank R.*, *Christopher K.* **Ingold**, and *Ian S.* **Wilson**, the nature of the alternating effect in carbon chains. Part VIII. The nitration of some benzylamine derivatives with special reference to the respective rôles of the ions, salts, and bases, 2440.
Gotts, *Reginald A.* See *William H.* **Mills**.
Gough, *George A. C.*, *Harold* **Hunter**, and *Joseph* **Kenyon**, the alcohols of the hydroaromatic and terpene series. Part V. The geometrical and optical isomerism of the methyl*cyclo*hexanols, 2052.
Graesser-Thomas, *Franz R.*, *John M.* **Gulland**, and *Robert* **Robinson**, derivatives of homocatechol. Part I., 1971.
Grant, *James*, obituary notice of, 3244.
Gray, *William H.*, the action of antimony trichloride upon diazotised diamines, 3174.
Green, *Albert*, the action of thionyl chloride on hydroxyanthraquinones. Part II. Quinizarin, 1428.
the action of thionyl chloride on hydroxyanthraquinones. Part III., 2198.
Green, *G. Melling*. See *A. O.* **Jones**.
Green, *George M.*, an automatic siphonic gas circulator, 500.
Green, *Thomas E.*, and *Cyril N.* **Hinshelwood**, the catalytic decomposition of nitric oxide at the surface of platinum, 1709.
Green, *Thomas E.* See also *Cyril N.* **Hinshelwood**.
Greene, *Herbert*, the 4- and 4′-methoxybenzoylbenzoins, 328.
Griffith, *Robert O.* See *Joseph W.* **Belton**.
Gulland, *John M.*, and *Robert* **Robinson**, derivatives of homocatechol. Part II., 1976.
Gulland, *John M.* See also *Franz R.* **Graesser-Thomas**.
Gyngell, *Eric S.*, the alkaline hydrolysis of esters in aqueous alcoholic solution. Part I. The interaction of phenoxides and aliphatic esters in alcoholic solution, 2484.

H.

Halévy, *Jacob*. See *Frederick* **Challenger**.
Hamid, *M. Abdul*, *Kirpal* **Singh**, and *Horace B.* **Dunnicliff**, ethyl hydrogen sulphate. Part II., 1098.
Hamid, *Mohammed A.*, heterogeneous equilibria between the sulphates and nitrates of sodium and potassium and their aqueous solutions. Part I. The ternary systems, 199.
heterogeneous equilibria between the sulphates and nitrates of sodium and potassium and their aqueous solutions. Part II. The quaternary system H_2O–Na_2SO_4–$NaNO_3$–K_2SO_4–KNO_3, 206.
Hammick, *Dalziel L.*, ω-mono- and dibromo-derivatives of quinaldine and nitroquinaldines and their products of hydrolysis, 1302.
Hammick, *Dalziel L.*, and *William E.* **Holt**, pseudo-ternary systems containing sulphur. Part I. Sulphur and quinoline, pyridine, and *p*-xylene, 1995.

Hammick, *Dalziel L.*, and *Michael* **Zvegintzov**, the rate of reaction between formic acid and iodine in aqueous solution, 1105.

Hammond, *Frederick*. See *Harold* **Burton**.

Handley, *Frederick W.* See *Herbert H.* **Hodgson**.

Harding, *Arthur J. I.* See *William* **Wardlaw**.

Hariharan, *Kalvoi V.* See *Charles S.* **Gibson**.

Harris, *Edgar R.* See *Samuel* **Glasstone**.

Harrison, *Harold A.*, unsymmetrically substituted dinitro- and diamino-derivatives in the stilbene and tolane series. Part II. The mode of addition of water to 3:4′-dinitro- and diamino-tolanes, 1232.

Harrison, *Harold A.*, and *Frank A.* **Royle**, the nitration of β-naphthoic acid and some new amino- and nitro-naphthoic acids, 84.

Harrison, *Harold A.*, and *Harold* **Wood**, unsymmetrically substituted dinitro- and diamino-derivatives in the stilbene and tolane series. Part I. The elimination of hydrogen chloride from 3:4′-dinitrostilbene dichloride, 577.

substituted cinnamic amides and acids, 1195.

Harrison, *Philip W. B.*, *Joseph* **Kenyon**, and *Henry* **Phillips**, the dependence of rotatory power on chemical constitution. Part XXIX. The resolution of sulphoxides into their optically active forms, 2079.

Harrison, *Philip W. B.*, *Joseph* **Kenyon**, and *John R.* **Shepherd**, the dependence of rotatory power on chemical constitution. Part XXVIII. *d-sec.*-Butylbenzene, 658.

Harrison, *William F.* See *Gilbert T.* **Morgan**.

Hartshorne, *Norman H.* See *Sydney R.* **Carter**.

Hartung, *Ernst J.*, studies with the microbalance. Part III. The filtration and estimation of very small amounts of material, 840.

studies with the microbalance. Part IV. The photochemical decomposition of silver iodide, 1349.

Hartwell, *Francis J.* See *Hubert F.* **Coward**.

Harvey, *John*, *Isidor M.* **Heilbron**, and *Edward D.* **Kamm**, the unsaponifiable matter from the oils of elasmobranch fish. Part III. Tetra*cyclo*squalene and the production of a new naphthalene hydrocarbon, 3136.

Hassell, *Albert*, and *Christopher K.* **Ingold**, the conditions underlying the formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. Part VIII. Products derived from pimelic acid. An application of Bischoff's dynamic hypothesis, 1465.

the chemistry of polycyclic structures in relation to their homocyclic unsaturated isomerides. Part VII. Tautomerism corresponding with that of nitrosophenol and quinone-oxime in the *bicyclo*pentane series, 1836.

Haworth, *Robert D.*, and *William H.* **Perkin**, *jun.*, the conversion of berberine into β-homochelidonine (α-*allo*cryptopine), 445.

synthesis of cryptopine and protopine, 1769.

Haworth, *Robert D.*, *William H.* **Perkin**, *jun.*, and *John* **Rankin**, resolution of *dl*-dicentrine, 29.

Haworth, *Robert D.*, *William H.* **Perkin**, *jun.*, and *Thomas S.* **Stevens**, the preparation of 3:4-methylenedioxyhomophthalic acid, 1764.

Haworth, *Robert D.* See also *Ray* **Campbell**.

Haworth, *Walter N.*, and *Edmund L.* **Hirst**, the structure of fructose, γ-fructose, and sucrose, 1858.

Haworth, *Walter N.*, and *William* **Maw**, sugar carbonates. Part II. Derivatives of arabinose and xylose, 1751.

Haworth, *Walter N.*, and *Vincent S.* **Nicholson**, the structure of lactones from simple sugars; trimethyl γ-arabonolactone and the supposed β-gluconolactone and β-mannonolactone, 1899.

Haworth, *Walter N.*, and *Stanley* **Peat**, the constitution of the disaccharides. Part XI. Maltose, 3094.

Haworth, *Walter N.*, and *William G.* **Sedgwick**, new crystalline forms of trimethyl glucose and dimethyl glucose, 2573.

Haworth, *Walter N.*, and *George C.* **Westgarth**, synthesis of derivatives of γ-xylose, 880.

Haworth, *Walter N.* See also *William* **Charlton**, *Conrad J. A.* **Cooper**, and *Harry D. K.* **Drew**.

Heap, *Tom*, and *Robert* **Robinson**, a synthesis of kaempferide and of *iso*rhamnetin, 2336.

Hedges, *Ernest S.*, experiments on the variation of the angles of crystals during growth, 791.

Hedges, *Ernest S.*, liquid-line corrosion, 831.
periodic phenomena at anodes of copper and silver, 1533.
an alternating-current cell, 1892.
periodic phenomena at anodes of magnesium, zinc, cadmium, mercury, tin, and lead, and at an unattackable anode, 2580.
the periodic electrochemical passivity of iron, cobalt, nickel, and aluminium, 2878.

Heilbron, *Isidor M.*, *Thomas P.* **Hilditch**, and *Edward D.* **Kamm**, the unsaponifiable matter from the oils of elasmobranch fish. Part II. The hydrogenation of squalene in the presence of nickel, 3131.

Heilbron, *Isidor M.*, *Edward D.* **Kamm**, and *William M.* **Owens**, the unsaponifiable matter from the oils of elasmobranch fish. Part I. A contribution to the study of the constitution of squalene (spinacene), 1630.

Heilbron, *Isidor M.*, and *Armad* **Zaki**, styrylbenzopyrylium salts. Part VII. The conversion of 7-methoxy-2:3-dimethylchromone into styrylpyrylium salts, 1902.

Heilbron, *Isidor M.* See also *Harold* **Atkinson**, and *John* **Harvey**.

Henderson, *Edward.* See *Alexander R.* **Normand**.

Henderson, *George G.*, *William* **M'Nab**, and *John M.* **Robertson**, the constituents of oil of supa; a new natural source of copaene, 3077.

Henderson, *George G.*, and *Alexander* **Robertson**, the oxidation of sabinol with hydrogen peroxide, 2761.

Henderson, *George G.*, and *John M.* **Robertson**, the chemistry of cadinene. Part II. Compounds related to cadinene, 2811.

Henderson, *George G.*, *John M.* **Robertson**, and *Carl A.* **Kerr**, the chemistry of the caryophyllene series. Part I., 62.

Henry, *Thomas A.*, and *Thomas M.* **Sharp**, mercuration of some alkylphenols and alkylphenolaldehydes, 2432.

Hewitt, *Leslie F.*, and *Harold* **King**, trypanocidal action and chemical constitution. Part IV. Arylamides of aminohydroxyphenylarsinic acids, 817.

Hewitt, *Leslie F.*, *Harold* **King**, and *William O.* **Murch**, trypanocidal action and chemical constitution. Part V. Arylsulphonamides of some phenylarsinic acids, 1355.

Hicks, *Cedric S.*, tautomerism in the thyroxin molecule, 643.

Hilditch, *Thomas P.*, the isomerism of the dihydroxystearic acids produced by oxidation of acids of the oleic and elaidic series, 1828.

Hilditch, *Thomas P.* See also *Isidor M.* **Heilbron**.

Hill, (*Miss*) *Ellen S.*, the reduction of ethyl dibenzylacetoacetate, 956.

Hinkel, *Leonard E.*, and *William R.* **Madel**, condensation of 3-bromo- and 3-nitro-4-dimethylaminobenzaldehyde with ethyl acetoacetate and ammonia, 161.

Hinshelwood, *Cyril N.*, and *Thomas E.* **Green**, the interaction of nitric oxide and hydrogen and the molecular statistics of termolecular gaseous reactions, 730.

Hinshelwood, *Cyril N.* See also *Thomas E.* **Green**, and *William K.* **Hutchison**.

Hirst, *Edmund L.*, the structure of the normal monosaccharides. Part IV. Glucose, 350.

Hirst, *Edmund L.*, and *Alexander K.* **Macbeth**, the structure of the normal monosaccharides. Part III. Rhamnose, 22.

Hirst, *Edmund L.* See also *Walter N.* **Haworth**.

Hiscocks, *Edward S.* See *John A. V.* **Butler**.

Hodges, *Francis W.*, the reaction between picryl chloride and pyridine in alcoholic solution, 2417.

Hodgson, *Herbert H.*, studies in the diphenyl series. Part II. The nitration of diphthalylbenzidine, 2384.

Hodgson, *Herbert H.*, and *Herbert G.* **Beard**, chloro-derivatives of *m*-hydroxybenzaldehyde, 147.
nitration of chlorinated 3-hydroxybenzaldehydes and some consequences of adjacent substitution, 2030.

Hodgson, *Herbert H.*, and *Faqir C.* **Gorowara**, studies in the diphenyl series. Part I. The isomeric 4:4′-dichloro-3:3′(2:3′?)- and 3:5′-dinitrodiphenyls, 1754.

Hodgson, *Herbert H.*, and *Frederick W.* **Handley**, studies in colour and constitution. Part I. The influence of the methylthiol group, alone and in conjunction with the methoxy-group, 542.

Hodgson, *Herbert H.*, and *Ernest* **Kilner**, preparation of 1-halogeno-2-nitronaphthalenes and 2-nitronaphthalene, 7.

Hodgson, *Herbert H.*, and *Francis H.* **Moore**, the nitration of *m*-bromophenol, 155.

nitrosation of phenols. Part III. Nitrosation of 4-halogeno-*o*- and -*m*-cresols and oximation of the 4-halogeno-2:5-toluquinones, 2036.

Hodgson, *Herbert H.*, and *John S.* **Wignall**, preparation of 3:5-dihalogenophenols, 2077.

preparation of the 5-halogenoresorcinols, 2826.

Hogg, *Arthur R.*, the ternary system sodium sulphide–sodium sulphate–water, 855.

Holderness, *Albert.* See *George H.* **Christie.**

Holmes, *Eric L.*, and *Christopher K.* **Ingold**, the nature of the alternating effect in carbon chains. Part IV. Some abnormal reactions as evidence of the incipient ionisation of certain hydrogen atoms in hydrocarbon radicals, 1305.

the nature of the alternating effect in carbon chains. Part VI. A study of the relative directive efficiencies of oxygen and fluorine in aromatic substitution, 1328.

Holmes, *Eric L.*, *Christopher K.* **Ingold**, and (*Mrs.*) *Edith H.* **Ingold**, the nature of the alternating effect in carbon chains. Part VII. A study of the relative directive efficiencies of oxygen and sulphur in aromatic substitution, 1684.

Holmes, *Eric L.* See also *Bernhard* **Flürscheim.**

Holmes, *Marshall*, the action of light on concentrated aqueous solutions of ammonium thiocyanate, 1690.

the alleged decomposition of aqueous ammonium nitrite solutions by light, 1898.

Holt, *William E.* See *Dalziel L.* **Hammick.**

Hoskins, *Charles R.* See *Harry M.* **Dawson.**

Howard, *Edward J.*, and *William H.* **Patterson**, the influence of dissolved salts on the mutual miscibility temperature of the systems ethyl alcohol or methyl alcohol–paraffins, 2787.

miscibility tests of dilute solutions of chromic chloride hexahydrates, 2791.

Humby, *Spencer R.*, and *Michael W.* **Perrin**, deposition of metallic zinc on the positive pole of a simple voltaic cell, 959.

Hume, *John*, and *Bryan* **Topley**, the density of calcium carbonate hexahydrate, 2932.

Hume, *John.* See also *Norman H.* **Chamberlain.**

Hume-Rothery, *William.* See *Bertram* **Lambert.**

Humphries, *James E.*, condensations involving reactive methyl groups in heterocyclic bases, 374.

Hunter, *Harold.* See *George A. C.* **Gough.**

Hunter, *Robert F.*, halogenation of 2:6-dimethylbenzbisthiazole and of 3:5-diphenylimino-2:4-diphenyltetrahydro-1:2:4-thiodiazole, 533.

bromination of some 5-substituted 1-phenylbenzthiazoles, 537.

aminobenzthiazoles. Part III. The tautomerism and unsaturation of the aminothiazole system, 1385.

aminobenzthiazoles. Part IV. The stability of the bromides of the 1-xylidinodimethylbenzthiazoles, 1401.

aminobenzthiazoles. Part V. Stability of the 1-alkylaminobenzthiazole bromides, 2951.

Hunter, *Robert F.*, and *Charles* **Soyka**, aminobenzthiazoles. Part VI. The addition of bromine to nascent tautomeric systems of the aminothiazole type and the mobility and unsaturation of the 5-bromo-1-alkylaminobenzthiazole system, 2958.

Hunter, *Robert F.* See also *George M.* **Dyson.**

Hurtley, *William R. H.*, and *Samuel* **Smiles**, *o*-dithiolbenzene, 1821.

2:2′-bis-1:3-benzdithiolene, 2263.

Hutchison, *William K.*, and *Cyril N.* **Hinshelwood**, the interaction of hydrogen and nitrous oxide on the surface of gold, 1556.

I.

Ing, *Harry R.*, and *Richard H. F.* **Manske**, a modification of the Gabriel synthesis of amines, 2348.

Ing, *Harry R.*, and *Robert* **Robinson**, the orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. Part I. The nitration of some derivatives of benzylamine, 1655.

Ingold, *Christopher K.*, and (*Mrs.*) *Edith H.* **Ingold**, the nature of the alternating effect in carbon chains. Part V. A discussion of aromatic substitution with special reference to the respective rôles of polar and non-polar dissociation; and a further study of the relative directive efficiencies of oxygen and nitrogen, 1310.

action of nitric acid on *S*-methylthioguaiacol, 3093.

Ingold, *Christopher K.*, and *Philip G.* **Marshall**, the structure of the benzene nucleus. Part V. Some *meso*-derivatives of anthracene, 3080.

Ingold, *Christopher K.*, and *Charles W.* **Shoppee**, constitution of the yellow sodium compounds formed from ethyl citraconate (or itaconate) and ethyl sodiomalonate, 1912.

Ingold, *Christopher K.*, *Charles W.* **Shoppee**, and *Jocelyn F.* **Thorpe**, the mechanism of tautomeric interchange and the effect of structure on mobility and equilibrium. Part I. The three-carbon system, 1477.

Ingold, *Christopher K.* See also *John W.* **Baker**, *Kenneth E.* **Cooper**, *Richard* **Gane**, *Frank R.* **Goss**, *Albert* **Hassell**, and *Eric L.* **Holmes**.

Ingold, (*Mrs.*) *Edith H.*, the specific heats of hydrocyanic acid, 26, 2016.

Ingold, (*Mrs.*) *Edith H.* See also *Kenneth E.* **Cooper**, *Eric L.* **Holmes**, and *Christopher K.* **Ingold**.

Irvine, (*Sir*) *James C.*, and *Ian M. A.* **Black**, the constitution of maltose, 862.

Irvine, (*Sir*) *James C.*, and *John* **Macdonald**, the constitution of polysaccharides. Part X. The molecular unit of starch, 1502.

Irvine, (*Sir*) *James C.*, and *George J.* **Robertson**, the constitution of polysaccharides. Part IX. The degradation of cellulose to an anhydrotrisaccharide, 1488.

Irvine, (*Sir*) *James C.*, and *Andrew F.* **Skinner**, the behaviour of mannose diacetone on methylation, 1089.

Iyer, *Subramania N.*, and *John L.* **Simonsen**, the catalytic hydrogenation of carone, 2049.

J.

James, *Frank.* See *Sydney R.* **Carter**.

Japp, *Francis R.*, obituary notice of, 1008.

Johnson, *John D. A.*, and *George A. R.* **Kon**, the chemistry of the three-carbon system. Part IX. The $\alpha\beta$–$\beta\gamma$-change in β-alkylcinnamic acids, 2748.

Johnston, *William.* See *Robert M.* **Caven**.

Jolly, *Victor G.*, and *Henry V. A.* **Briscoe**, a differential method for the measurement of the vapour pressure of liquids, 2154.

Jones, *A. O.*, and *G. Melling* **Green**, the reaction between aluminium, iodine, ethyl alcohol, and water; preparation of ethyl iodide, 2760.

Jones, *Edward C.* See *Samuel* **Glasstone**.

Jones, *Francis*, obituary notice of, 1020.

Jones, *Griffith G.*, and *Thomas M.* **Lowry**, studies of dynamic isomerism. Part XXI. The velocity of mutarotation of tetramethylglucose and of tetra-acetylglucose in aqueous acetone, 720.

Jones, *Griffith G.* See also *Ronald G. W.* **Norrish**.

Jones, *Thomas G. H.*, olefinic terpene ketones from the volatile oil of flowering *Tagetes glandulifera*. Part II., 2767.

Jones, *William J.* See *David G. R.* **Bonnell**.

K.

Kamm, *Edward D.* See *John* **Harvey**, and *Isidor M.* **Heilbron**.

Kanga, *Darab D.*, *Panchandana R.* **Ayyar**, and *John L.* **Simonsen**, conessine, 2123.

Kay, *Francis W.*, and *Noel* **Stuart**, the stereochemistry of the hydronaphthalenes. Part I. Decahydro-β-naphthamides, 3038.

Kellett, *Richard E.* See *Gilbert T.* **Morgan**.

Kenner, *James.* See *Harold* **Burton**, and *George H.* **Christie**.

Kenyon, *Joseph*, and *Percy H.* **Robinson**, investigations in the diphenyl series. Part IV. Halogenation of 4-aminodiphenyl, 3050.

Kenyon, *Joseph.* See also *Francis H.* **Banfield**, *Frank* **Bell**, *Allan* **Domleo**, *George A. C.* **Gough**, and *Philip W. B.* **Harrison**.

Kerr, *Carl A.* See *George G.* **Henderson**.

Kerr, *Robert N.*, the dielectric constants of mixtures of organic liquids, 2796.

Kilner, *Ernest.* See *Herbert H.* **Hodgson**.

King, *Frederick E.*, and *James R.* **Partington**, the solubility of sodium iodide in ethyl alcohol, 20.
the vapour pressures of chlorine dioxide, 925.
King, *Harold.* See *Leslie F.* **Hewitt.**
Kipping, *Frederic B.*, and (*Sir*) *William J.* **Pope**, the resolution of *dl*-alanine and the formation of *trans*-2:5-dimethylpiperazine, 494.
preparation and resolution of *dl-cis*-2:5-dimethylpiperazine, 1076.
Kleist, *Leslie L.* See *George A.* **Elliott.**
Knecht, *Edmund*, obituary notice of, 1021.
Kon, *George A. R.*, the chemistry of the three-carbon system. Part V. The alkylation of unsaturated ketones, 1792.
Kon, *George A. R.*, and *John H.* **Nutland**, the chemistry of the three-carbon system. Part X. The mobility of some cyclic ketones, 3101.
Kon, *George A. R.*, and *Muhammad* **Qudrat-i-Khuda**, preparation of *cis*-*o*-carboxy*cyclo*hexaneacetic acid, 3071.
Kon, *George A. R.*, and *Eric A.* **Speight**, the chemistry of the three-carbon system. Part VII. Derivatives of malonic acid, 2727.
Kon, *George A. R.* See also *Maurice D.* **Farrow**, and *John D. A.* **Johnson.**
Kracovski, *Jacob.* See *Ernest H.* **Farmer.**
Krishnamurti, *K.* See *Jnanendra N.* **Mukherjee.**
Krishnamurti, *Subramonia*, the precipitation of cadmium sulphide from aqueous solutions of cadmium chloride in the presence of hydrochloric acid and other chlorides, 1549.

L.

Lambert, *Bertram*, and *William* **Hume-Rothery**, studies of precipitated solids. Part I. Strontium sulphate, 2637.
Lambert, *Bertram*, and *Robert J.* **Schaffer**, studies of precipitated solids. Part II. Calcium sulphate, 2648.
Lang, *William R.*, obituary notice of, 1024.
Lanyon, *John A.* See *Malcolm P.* **Applebey.**
Lapworth, *Arthur.* See *George N.* **Burkhardt.**
Law, *Kenneth K.*, some new organo-tin compounds, 3243.
Lea, *Frederick M.* See *Sydney R.* **Carter.**
Lea, *Thomas R.*, and *Robert* **Robinson**, the relative directive powers of groups of the forms RO and RR′N in aromatic substitution. Part V. The nitration of *p*-methoxydiphenyl ether, 411.
the fission of some methoxylated benzophenones, 2351.
Leeper, *Geoffrey W.* See *William* **Davies.**
Le Fèvre, *Raymond J. W.*, and *Eustace E.* **Turner**, orientation effects in the diphenyl series. Part II. The constitution of Bandrowski's dinitrobenzidine, 1759.
orientation effects in the diphenyl series. Part III. The mononitro-4:4′-dihalogenodiphenyls and some allied compounds, 2041.
the space formula of diphenyl, 2476.
Lenher, *Sam*, the adsorption of water vapour on a plane fused quartz surface; the isosteric heats of adsorption of water on silica and on platinum, 1785.
Levin, (*Miss*) *Esther.* See *Frederick M.* **Rowe.**
Lewis, *Bernard*, and *Eric K.* **Rideal**, the Budde effect in bromine. Part I. The photoactive constituent of wet bromine, 583.
the Budde effect in bromine. Part II. The kinetics of the reaction and the light absorption of wet and of dry bromine, 596.
Lewis, *Neil B.* See *Nevil V.* **Sidgwick.**
Lewis, *William J.*, obituary notice of, 3245.
Liefde, *Willem de.* See *Andreas* **Smits.**
Linstead, *Reginald P.*, and *Leslie T. D.* **Williams**, the chemistry of the three-carbon system. Part VIII. Tautomeric systems terminated by a phenyl group, 2735.
Livingstone, *Alexander Y.* See *John A.* **Cranston.**
Lloyd, *William V.* See *Henry J. S.* **Sand.**
Lowry, *Thomas M.*, and *Glyn* **Owen**, studies of valency. Part V. Absorption spectra of halogen and sulphonic derivatives of camphor: origin of the ketonic absorption band, 606.
Lowry, *Thomas M.*, and (*Miss*) *Rose R.* **Sass**, studies of valency. Part VI. General and selective absorption of halogen derivatives of methane; the origin of general absorption, 622.
Lowry, *Thomas M.* See also *Irvine J.* **Faulkner**, and *Griffith G.* **Jones.**

M

Macallum, *Alexander D.*, synthesis of iodine compounds of the salvarsan group, 1645.

McBain, *James W.*, and *William J.* **Elford**, the equilibria underlying the soap-boiling processes; the system potassium oleate–potassium chloride–water, 421.

McBain, *James W.*, and *Albert V.* **Pitter**, the relative concentrations of various electrolytes required to salt out soap solutions, 893.

Macbeth, *Alexander K.*, *Thomas H.* **Nunan**, and *David* **Traill**, the labile nature of the halogen atom in organic compounds. Part XII. Halogen compounds of barbituric acids, 1248.

Macbeth, *Alexander K.* See also *Edmund L.* **Hirst**.

McClelland, *Ernest W.*, and *Alban J.* **Gait**, derivatives of 2-keto-1:2-dihydrobenz*iso*thiazole, 921.

McCombie, *Hamilton.* See *William* **Blakey**.

MacCulloch, (*Mrs.*) *I. F.* See **Semple**.

Macdonald, *John.* See (*Sir*) *James C.* **Irvine**.

McDowall, *Frederick H.*, preparation of ethylene bromohydrin, 499.

McGookin, *Alexander*, and *Donald J.* **Sinclair**, the isomerism of the styryl alkyl ketones. Part III. Methoxy-2- and -4-hydroxystyryl alkyl ketones, 1578.

McHutchison, *John P.*, the temperature of maximum density of alcohol–water mixtures, 1898.

McKenzie, *Alexander*, and *Walter S.* **Dennler**, the dehydration of glycols derived from α-naphthylglycollic acid, 1596.

McKenzie, *Alexander*, *Robert* **Roger**, and *George O.* **Wills**, elimination of the amino-group of tertiary amino-alcohols. Part III. A new method for the preparation of optically active ketones, 779.

McKeown, *Andrew.* See *Joseph W.* **Belton**.

McMath, (*Miss*) *Ann M.* See *John* **Read**.

McMillan, *Andrew.* See *Allan M.* **Drummond**.

M'Nab, *William.* See *George G.* **Henderson**.

McOwan, *George*, the constitution of sucrose. Part I. Oxidation of tetramethyl γ-fructose, 1737.

the constitution of sucrose. Part II. Evidence contributed by the oxidation of *d*-arabinose, 1747.

McVicker, *William H.*, *Joseph K.* **Marsh**, and *Alfred W.* **Stewart**, Tesla-luminescence spectra. Part VI. Some amino-derivatives, 17.

Madden, *F. C.* See *William E.* **Garner**.

Madel, *William R.* See *Leonard E.* **Hinkel**.

Malkin, *Thomas.* See *Stephen H.* **Piper**.

Maltby, *John G.*, the classification of the sugars, 1629.

Manjunath, *Basavalingaiah L.*, and *Sydney G. P.* **Plant**, derivatives of tetrahydrocarbazole. Part VI. Compounds derived from 6-methyltetrahydrocarbazole, 2260.

Mann, *Frederick G.*, the complex salts of αβγ-triaminopropane with copper and platinum, 2681.

Mann, *Frederick G.*, and (*Sir*) *William J.* **Pope**, the complex salts of ββ′β″-triaminotriethylamine with nickel and palladium, 482.

γγ′γ″-triaminotripropylamine and its complex compounds with nickel, 489.

the configuration of the bistriaminopropane metallic complexes, 2675.

Manning, *John*, preparation of nickel membranes for ultrafiltration, 1127.

Manske, *Richard H. F.* See *Harry R.* **Ing**.

Marsh, *Joseph K.* See *Norman S.* **Capper** and *William H.* **McVicker**.

Marshall, *Philip G.* See *Christopher K.* **Ingold**.

Mason, *Frederick A.*, a synthesis of 1:2-dihydroquinaldine, 955.

Matthews, *Ernest*, the interaction of sulphur dioxide and hydrogen sulphide, 2270.

Matthews, *Marcus A.*, reactions of the *meso*-hydroxyanthrones, 236.

Maw, *William.* See *Walter N.* **Haworth**.

Maxted, *Durban R.*, the oxidation of tartaric acid by solutions of silver salts, 2178.

Mayes, *Horace A.*, and *James R.* **Partington**, thionyl bromide and Besson's supposed thionyl chlorobromide, 2594.

Menon, *Kottiazath N.* See *Charles S.* **Gibson**.

Menzies, *Robert C.* See (*Miss*) *Christina M.* **Fear**.

Millott, *John O.* See *Edmund B. R.* **Prideaux**.

Mills, *William H.*, and *Reginald A.* **Gotts**, optical activity dependent on co-ordinated beryllium, copper, and zinc, 3121.

Mitchell, *Alec D.*, the reaction between hydroxylamine and ferric chloride, 336.

Mitchell, *Robert K. S.* See *Harold G.* **Rule.**

Mitchell, *Stotherd*, a method for determining the solubility of sparingly soluble substances, 1333.

Mitra, *Subhendu K.* See *Jnanendra N.* **Mukherjee.**

Moore, *Francis H.* See *Herbert H.* **Hodgson.**

Morgan, *Gilbert T.*, and *Francis H.* **Burstall**, researches on residual affinity and co-ordination. Part XXVII. Ethylenediammine copper salts, 2018.

Morgan, *Gilbert T.*, *Sydney R.* **Carter**, and *William F.* **Harrison**, researches on residual affinity and co-ordination. Part XXVIII. Thermal measurements on derivatives of cupric iodide, 2027.

Morgan, *Gilbert T.*, and *Richard E.* **Kellett**, interactions of tellurium tetrachloride and aryl alkyl ethers. Part II., 1080.

Morgan, *Gilbert T.*, and *Charles R.* **Porter**, carboxylated β-diketones, 1256.

Morgan, *Gilbert T.*, and *J. D. Main* **Smith**, researches on residual affinity and co-ordination. Part XXVI. A quadridentate group in combination with bivalent metals, 912.

Morgan, *Gilbert T.*, and *Cyril J. A.* **Taylor**, keto-enol isomerism of ethylenebisacetylacetone, 43.

Morgan, *Gilbert T.*, and *Reuben W.* **Thomason**, nitration of fluorene; 2:5-dinitrofluorene, 2691.

Morgan, *Walter T. J.*, butyl esters of the simpler amino-acids. Part I., 79.

Morton, *Richard A.*, absorption spectra of mesityl oxide, 719.

Morton, *Richard A.*, and *Edward* **Rogers**, absorption spectra and tautomerism. Part II. Ethyl mesityloxidoxalate, formylphenylacetate, and diacetylsuccinate, 713.

Morton, *Richard A.*, and *William C. V.* **Rosney**, absorption spectra and tautomerism. Part I. Keto-enol tautomerism; ethyl acetoacetate, acetylacetone, and α-benzoylcamphor, 706.

Mounfield, *James D.*, and *John K.* **Wood**, the effect of heat on chloral hydrate, 498.

Müller, *Heinz*, and *Albert J.* **Bradley**, copper hydride and its crystal structure, 1669.

Mukherjee, *Jnanendra N.*, *Bivas C.* **Ghosh**, *K.* **Krishnamurti**, *Gajendra N.* **Ghosh**, *Subhendu K.* **Mitra**, and *Bankim C.* **Roy**, interaction between hydrated silica and neutral electrolytes in its relation to the nature of hydrolytic adsorption, 3023.

Murch, *William O.* See *Leslie F.* **Hewitt.**

N.

Nair, *Srikumaran U.*, and *John L.* **Simonsen**, derivatives of acenaphthpyridine. Part I., 3140.

Nicholson, *Vincent S.* See *Walter N.* **Haworth.**

Nijhawan, *Sukh D.* See *Horace B.* **Dunnicliff.**

Nimkar, *Vishvanath K.* See *Robert* **Forsyth.**

Nolan, *Thomas J.*, *David D.* **Pratt**, and *Robert* **Robinson**, a synthesis of pyrylium salts of anthocyanidin type. Part XI. A synthesis of peonidin chloride, 1968.

Normand, *Alexander R.*, *John D. M.* **Ross**, and *Edward* **Henderson**, an *X*-ray investigation of the normal saturated dicarboxylic acids and their ethyl esters, 2632.

Norris, *Woodford S. G. P.*, *cyclo*hexane-*spirocyclo*hexane, 245.

Norris, *Woodford S. G. P.* See also *Stanley F.* **Birch.**

Norrish, *Ronald G. W.*, and *Griffith G.* **Jones**, studies of valency. Part VII. Surface polarity and the reaction of ethylene and chlorine; the effect of the adsorbed water layer, 55.

Numbers, (*Miss*) *Annie H.* See *Harold G.* **Rule.**

Nunan, *Thomas H.* See *Alexander K.* **Macbeth.**

Nutland, *John H.* See *George A. R.* **Kon.**

O.

Oakeshott, *Stephen H.*, and *Sydney G. P.* **Plant**, some reactions of 1-*p*-toluidino*cyclo*pentane-1-carboxylic acid; a new carbazole synthesis, 1210.

Owen, *Glyn.* See *Thomas M.* **Lowry.**

Owens, *William M.* See *Isidor M.* **Heilbron.**

Oxford, *Albert E.*, new derivatives of guaiacol and veratrole substituted in the 3- and 6-positions, 2004.

Oxford, *Albert E.*, and *Robert* **Robinson**, the relative directive powers of groups of the forms RO and RR'N in aromatic substitution. Part II. The nitration of some 2-benzyloxyanisoles substituted in the benzyl group, 383.

Oxford, *Albert E.* See also *James* **Allan**.

P.

Packer, *John*, and *Albert C. D.* **Rivett**, the binary system barium iodide–water, 1061.

Packer, *John*, and *Jocelyn F.* **Thorpe**, the chemistry of the glutaconic acids. Part XIX. A consequence of mobility, 1199.

Packer, *John*. See also *Henry G.* **Denham**.

Parkes, *George D.* See *Frederick D.* **Chattaway**.

Partington, *James R.*, the specific heats of hydrogen cyanide, 1559.

Partington, *James R.*, and *Sidney K.* **Tweedy**, the hydrates of chromic nitrate, 1142.

Partington, *James R.* See also *Frederick E.* **King**, and *Horace A.* **Mayes**.

Paterson, *H. A.* See *R. Christie* **Smith**.

Patterson, *Thomas S.*, *James D.* **Fulton**, and *Jean M.* **Semple**, studies in optical superposition. Part VII. The bornyl dimethoxysuccinates, 3224.

Patterson, *William H.* See *Edward J.* **Howard**.

Peat, *Stanley*. See *William* **Charlton**, *Conrad J. A.* **Cooper**, and *Walter N.* **Haworth**.

Perkin, *William H., jun.*, *Jnanendra N.* **Rây**, and *Robert* **Robinson**, experiments on the synthesis of brazilin and hæmatoxylin and their derivatives. Part I. Veratrylidene-7-methoxychromanone and an account of a new synthesis of some benzopyrylium salts, 911.

Perkin, *William H., jun.*, and *Leon* **Rubenstein**, 3:4- and 2:5-dimethoxyphenylhydrazine, 357.

Perkin, *William H., jun.*, and *William G.* **Sedgwick**, tetrahydroacridine, octahydroacridine, and their derivatives. Part II. Resolution of the octahydroacridines (A) and (B), 438.

Perkin, *William H., jun.*, and *Victor M.* **Trikojus**, synthesis of some derivatives of methylenedioxybenzene, 2925.

Perkin, *William H., jun.* See also *Ray* **Campbell**, and *Robert D.* **Haworth**.

Perrin, *Michael W.* See *Spencer R.* **Humby**.

Peters, *Arnold T.* See *Frederick* **Challenger**.

Phillips, *Henry*. See *Philip W. B.* **Harrison**.

Phillips, *Montague A.*, the crotonic acid series. Part I. Nitrogen derivatives of crotonic acid, 2979.

Piper, *Stephen H.*, *Thomas* **Malkin**, and *Harold E.* **Austin**, an *X*-ray study of some structural modifications of long-chain compounds, 2310.

Pitter, *Albert V.* See *James W.* **McBain**.

Plant, *Sydney G. P.* See (*Miss*) *Winifred M.* **Collar**, *Basavalingaiah L.* **Manjunath**, and *Stephen H.* **Oakeshott**.

Plenderleith, *H. J.* See *A. Chaston* **Chapman**.

Pollard, *Alfred*, and *Robert* **Robinson**, the alleged nitration of *S*-methylthioguaiacol, 3090.

Pollard, *William B.*, action of mercurous nitrate on chloroauric acid, 529.

the doubtful existence of aurous oxide, 1347.

Pope, *Frank G.*, obituary notice of, 1025.

Pope, (*Sir*) *William J.* See *Frederic B.* **Kipping**, and *Frederick G.* **Mann**.

Porter, *Charles R.* See *Gilbert T.* **Morgan**.

Potter, *Charles E.*, obituary notice of, 1027.

Pratt, *David D.* See *Thomas J.* **Nolan**.

Price, *Tudor W.*, the decomposition of substituted carbamyl chlorides by hydroxy-compounds. Part II. The influence of the hydroxy-compound, 653.

the decomposition of substituted carbamyl chlorides by hydroxy-compounds. Part III. The influence of substituent groups, 3230.

Prideaux, *Edmund B. R.*, and *John O.* **Millott**, action of hydrogen fluoride on compounds of selenium and tellurium. Part I. Selenium dioxide, 167.

the action of hydrogen fluoride on compounds of selenium and tellurium. Part II. Tellurium dioxide, 520.

Prideaux, *Edmund B. R.*, and *Edwin C.* **Roper**, hydrofluozirconic acid and the analysis of zirconium fluoride, 898.

Pugh, *William*, germanium. Part III. Salts of germanic acid, 2828.

Pugh, *William*, and *John S.* **Thomas**, germanium. Part II. Germanium tetrachloride and its ammonia compounds, 1051.
Puri, *Amar N.* See *Bawa K.* **Singh**.
Purvis, *John E.*, the absorption spectra of various derivatives of salicylic acid, 775.
Pyman, *Frank L.* See *Robert* **Forsyth**.

Q.

Qudrat-i-Khuda, *Muhammad.* See *George A. R.* **Kon**.

R.

Raikes, *Humphrey R.*, *Albert F.* **Yorke**, and *Frederick K.* **Ewart**, the equivalent conductivity of solutions of sodium hydroxide and the mobility of the hydroxyl ion, 630.
Raikes, *Humphrey R.* See also *Frederick K.* **Ewart**.
Rankin, *John.* See *Robert D.* **Haworth**.
Rao, *Keshaviah A. N.* See *Martin O.* **Forster**.
Ray, *Jnanendra N.* See *William H.* **Perkin**, *jun.*, and *Monmohan* **Sen**.
Read, *John*, (*Miss*) *Alison M. R.* **Cook**, and (*Miss*) *Mary I.* **Shannon**, researches in the menthone series. Part III. Optically inactive menthylamines, 2223.
Read, *John*, and (*Miss*) *Ann M.* **McMath**, a new method of diagnosing potential optical activity. Part II. The optical activity of chlorobromoacetic acid, 2183.
the optical resolution of chlorosulphoacetic acid, 2192.
Read, *John*, and *George J.* **Robertson**, researches in the menthone series. Part II. Optically active menthones and menthylamines, 2209.
Read, *John.* See also *John C.* **Earl**.
Reade, *Thomas H.*, quaternary ammonium perhalides, 2528.
Reade, *Thomas H.* See also (*Miss*) *Margaret F.* **Aitken**.
Reeve, *Lewis.* See *Arthur J.* **Allmand**.
Reilly, *Joseph*, and *Peter J.* **Drumm**, aminopropyl-1:2:4-triazoles, 1729.
Report of the Council, 962.
Richardson, *Donald H.*, the action of alcoholic potassium hydroxide upon chloronitrobenzene, 522.
Richardson, *Henry L.* See *Ernest H.* **Farmer**.
Rideal, *Eric K.*, and (*Miss*) *Winifred M.* **Wright**, low temperature oxidation at charcoal surfaces. Part II. The behaviour of charcoal in the presence of promoters, 1813.
low temperature oxidation at charcoal surfaces. Part III. The behaviour of blood charcoal and the influence of temperature on the reaction rate, 3182.
Rideal, *Eric K.* See also *Bernard* **Lewis**, and *Eric J. B.* **Willey**.
Riley, *Harry L.*, and *Herbert B.* **Baker**, the determination of the atomic weight of silver by the direct ratio of silver to oxygen in silver oxide, 2510.
Rivett, *Albert C. D.*, the constitution of magnesium acetate solutions, 1063.
Rivett, *Albert C. D.* See also *John* **Packer**.
Riwlin, *Rassa*, studies in adsorption by an optical method; fixation of methylene-blue by yeast-phosphoprotein sol within the disperse phase, 2300.
Riwlin, *Rassa.* See also *Andor* **Fodor**.
Roberts, *Elwyn*, and *Eustace E.* **Turner**, 10-chlorophenthiarsine, and its rate of formation from *o*-phenylthiolphenyldichloroarsine, 1207.
Roberts, *Elwyn*, *Eustace E.* **Turner**, and *Frank W.* **Bury**, *as*-chlorotetrahydroarsinoline and some quaternary arsonium compounds, 1443.
Robertson, *Alexander*, and *Robert* **Robinson**, experiments on the synthesis of anthocyanins. Part I., 1713.
a synthesis of pyrylium salts of anthocyanidin type. Part IX. Some hydroxyflavylium salts, 1951.
Robertson, *Alexander.* See also *George G.* **Henderson**.
Robertson, *George J.* See (*Sir*) *James C.* **Irvine**, and *John* **Read**.
Robertson, *John M.* See *David T.* **Gibson**, and *George G.* **Henderson**.
Robinson, (*Mrs.*) *Gertrude M.*, and *Robert* **Robinson**, synthesis of certain higher aliphatic compounds. Part II. The hydration of stearolic acid, 2204.
Robinson, *Percy H.* See *Frank* **Bell**, and *Joseph* **Kenyon**.
Robinson, *Percy L.*, and *Harold C.* **Smith**, a comparison of the atomic weights of silicon from different sources, 1262.
the absolute density and coefficient of expansion of silicon tetrachloride, 3152.

Robinson, *Percy L.*, *Harold C.* **Smith,** and *Henry V. A.* **Briscoe,** the hydrolytic action of low-pressure superheated steam on salts of the alkaline-earth metals, 836.

Robinson, *Percy L.* See also *Henry V. A.* **Briscoe.**

Robinson, *Robert*, and *Junzo* **Shinoda,** synthetical experiments in the phenanthrene group of the alkaloids. Part I., 1987.

Robinson, *Robert*, and *John C.* **Smith,** the relative directive powers of groups of the forms RO and RR′N in aromatic substitution. Part III. The nitration of some *p*-alkyloxyanisoles, 392.

Robinson, *Robert*, and *Sidney* **Thornley,** 3-methoxy-2-phenylindole and 3-benzoylamino-2-phenylindole, 3144.

Robinson, *Robert*, and *Krishnasami* **Venkataraman,** a synthesis of acacetin and certain other derivatives of flavone, 2344.

Robinson, *Robert*, and (*Miss*) *Helen* **West,** derivatives of 1-benzyltetrahydro*iso*quinoline, 1985.

Robinson, *Robert.* See also *James* **Allan,** *Wilson* **Baker,** *William* **Bradley,** *Robert S.* **Cahn,** *Constant van* **Duin,** (*Miss*) *Elisabeth S.* **Gatewood,** *Frank H.* **Gornall,** *Franz R.* **Graesser-Thomas,** *John M.* **Gulland,** *Tom* **Heap,** *Harry R.* **Ing,** *Thomas R.* **Lea,** *Thomas J.* **Nolan,** *Albert E.* **Oxford,** *William H.* **Perkin,** *jun.*, *Alfred* **Pollard,** *Alexander* **Robertson,** and (*Mrs.*) *Gertrude M.* **Robinson.**

Roger, *Robert.* See *Alexander* **McKenzie.**

Rogers, *Cecil W.*, the interaction between copper and sulphuric acid, 254.

Rogers, *Edward.* See *Richard A.* **Morton.**

Roper, *Edwin C.* See *Edmund B. R.* **Prideaux.**

Rosney, *William C. V.* See *Richard A.* **Morton.**

Ross, *John.* See *Ernest H.* **Farmer.**

Ross, *John D. M.*, and *Ian C.* **Somerville,** melting-point curves of optical isomerides in the camphor series, 2770.

Ross, *John D. M.* See also *Alexander R.* **Normand.**

Rothstein, *Eugene*, and *Jocelyn F.* **Thorpe,** formation and stability of *spiro*-compounds. Part XIII. *spiro*-Compounds from the substituted lævulic acids, 2011.

Rowe, *Frederick M.*, (*Miss*) *Esther* **Levin,** *Alan C.* **Burns,** *John S. H.* **Davies,** and *Wolfe* **Tepper,** a new reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. Part I. Preparation of phthalazine, phthalazone, and phthalimidine derivatives from 4′-nitrobenzene-2-naphthol-1-diazosulphonate, 690.

Rowell, *Sydney W.* See *Alexander S.* **Russell.**

Roy, *Bankim C.* See *Jnanendra N.* **Mukherjee.**

Royle, *Frank A.* See *Harold A.* **Harrison.**

Rubenstein, *Leon*, substitution in vicinal trisubstituted benzene derivatives. Part IV., 648.

Rubenstein, *Leon.* See also *William H.* **Perkin,** *jun.*

Rubli, *Hannes.* See *John B.* **Shoesmith.**

Rule, *Harold G.*, and *Robert K. S.* **Mitchell,** optical activity and the polarity of substituent groups. Part V. *sec.*-β-Octyl esters of some substituted acetic acids and their behaviour towards solvents, 3202.

Rule, *Harold G.*, and (*Miss*) *Annie H.* **Numbers,** optical activity and the polarity of substituent groups. Part IV. *sec.*-β-Octyl esters of *o*-, *m*-, and *p*-methoxy- and nitro-benzoic acids, 2116.

Rule, *Harold G.*, and *John* **Smith,** optical activity and the polarity of substituent groups. Part III. Menthyl acetophenone-*o*-carboxylate, 553.

Rushbrooke, *J. E.* See *William E.* **Garner.**

Russell, *Alexander S.*, air oxidation of titanous sulphate solution; vanadous sulphate, a new and powerful reducing agent, 497.

Russell, *Alexander S.*, *Derek C.* **Evans,** and *Sydney W.* **Rowell,** the order of removal of manganese, chromium, iron, cobalt, and nickel from amalgams, 1872.

Russell, *Alexander S.*, and *Sydney W.* **Rowell,** the positions of tungsten and molybdenum in the normal potential series, 1881.

S.

Sand, *Henry J. S.*, and *William V.* **Lloyd,** arrangement for alternating current electrolysis, 2971.

Sass, (*Miss*) *Rose R.* See *Thomas M.* **Lowry.**

Sayce, *Leonard A.*, and *Henry V. A.* **Briscoe**, critical temperature of mercury, 957.
the dielectric constants of some liquids and liquid mixtures, 2623.
Scarborough, *Harold A.*, and *William A.* **Waters**, the chlorination and bromination of 4-aminodiphenyl, 557.
Scarborough, *Harold A.* See also *William* **Blakey**.
Scarf, *Frank.* See *Charles E.* **Wood**.
Schaffer, *Robert J.* See *Bertram* **Lambert**.
Schoenmaker, *Pieter.* See *Andreas* **Smits**.
Sedgwick, *William G.* See *Walter N.* **Haworth**, and *William H.* **Perkin**, *jun.*
Semple, *Jean.* See *Thomas S.* **Patterson**.
Sen, *Monmohan*, and *Jnanendra N.* **Rây**, *N*-alkylated amidines, 646.
synthesis in the thianthren series. Part II., 1139.
Shannon, (*Miss*) *Mary I.* See *John* **Read**.
Sharp, *Thomas M.* See *Thomas A.* **Henry**.
Shepherd, *John R.* See *Philip W. B.* **Harrison**.
Shepherd, *Rodney T.* See *David L.* **Chapman**.
Shinoda, *Junzo.* See *Robert* **Robinson**.
Shoesmith, *John B.*, and *Hannes* **Rubli**, 5-methoxy-α-naphthaldehyde, 3241.
Shoesmith, *John B.*, and *Robert H.* **Slater**, preparation, hydrolysis, and reduction of the fluoro-, chloro-, and bromo-benzyl bromides, 214.
Shoesmith, *John B.*, *Charles E.* **Sosson**, and *Robert H.* **Slater**, the isomeric fluorobenzaldehydes and their derivatives, 2760.
Shoesmith, *John B.*, and *William E.* **Taylor**, the preparation and hydrolysis of the isomeric azoxybenzyl bromides, 2832.
Shoppee, *Charles W.* See *Christopher K.* **Ingold**.
Sidgwick, *Nevil V.*, and *Neil B.* **Lewis**, the solubility of beryllium oxide in solutions of its salts, 1237.
conductivities of some organic salts of beryllium, 2538.
Simonsen, *John L.* See *Charles S.* **Gibson**, *Subramania N.* **Iyer**, *Darab D.* **Kanga**, and *Srikumaran U.* **Nair**.
Simpson, *Ian A.* See *Stanley G.* **Willimott**.
Sinclair, *Donald J.* See *Alexander* **McGookin**.
Singh, *Bawa K.*, and *Amar N.* **Puri**, studies on the dependence of optical rotatory power on chemical constitution. Part VI. Rotatory powers of phenyl, *o*-, *m*-, *p*-tolyl and β-naphthyl derivatives of *d*-camphorimide and *d*-camphoramic acid, 504.
Singh, *Kirpal.* See *M. Abdul* **Hamid**.
Skinner, *Andrew F.* See (*Sir*) *James C.* **Irvine**.
Slater, *Robert H.* See *John B.* **Shoesmith**.
Smiles, *Samuel.* See *Leslie G. S.* **Brooker**, *Reginald* **Child**, and *William R. H.* **Hurtley**.
Smith, *Frederick J.* See *David R.* **Boyd**.
Smith, *Gilbert F.* See *Frederick G.* **Soper**.
Smith, *Harold C.* See *Percy L.* **Robinson**.
Smith, *John.* See *Harold G.* **Rule**.
Smith, *John C.* See *James* **Allan**, *Constant van* **Duin**, and *Robert* **Robinson**.
Smith, *J. D. Main.* See *Gilbert T.* **Morgan**.
Smith, *R. Christie*, and *H. A.* **Paterson**, determination of the rate of hydrolysis of sparingly soluble esters, 940.
Smits, *Andreas*, the influence of intensive drying on inner equilibria. Part II., 2655.
Smits, *Andreas*, *Willem de* **Liefde**, *Emanuel* **Swart**, and *Antony* **Claassen**, the influence of intensive drying on inner equilibria. Part III., 2657.
Smits, *Andreas*, and *Pieter* **Schoenmaker**, the complexity of the solid state. Parts III. and IV. The behaviour of pure sulphur trioxide. Parts II. and III., 1108.
Somerville, *Ian C.* See *John D. M.* **Ross**.
Soper, *Frederick G.*, and *Gilbert F.* **Smith**, the halogenation of phenols, 1582.
Sørensen, *Søren P. L.*, the composition and characterisation of genuine proteins, 2995.
Sosson, *Charles E.* See *John B.* **Shoesmith**.
Soyka, *Charles.* See *George M.* **Dyson**, and *Robert F.* **Hume**.
Speight, *Eric A.* See *George A. R.* **Kon**.
Stephen, *Herbert W.*, and *Forsyth J.* **Wilson**, some thiazole derivatives. Part I., 2531.
Stephenson, *George E.* See *Henry V. A.* **Briscoe**.
Stevens, *Thomas S.* See *Robert D.* **Haworth**.

Stewart, *Alfred W.* See *William H.* **McVicker.**
Stuart, *Noel.* See *Francis W.* **Kay.**
Such, *John E.* See *Charles E.* **Wood.**
Sugden, *James N.*, the hydration of strong electrolytes, the viscosity of their aqueous solutions, and the dilution law, 174.
Sugden, (*Miss*) *Ruth*, the system ammonium acetate–acetic acid–water, 960.
Sugden, *Samuel*, and *Montague* **Williams**, an experimental study of protective colloids. Part I. The influence of concentration, 2424.
Sugiura, *Shigetake*, obituary notice of, 3246.
Swart, *Emanuel.* See *Andreas* **Smits.**
Sword, *James.* See *David T.* **Gibson.**

T.

Taylor, *Cyril J. A.* See *Gilbert T.* **Morgan.**
Taylor, *Robert L.*, obituary notice of, 1029.
Taylor, *Thomas W. J.*, and (*Miss*) *Elinor K.* **Ewbank**, the metallic compounds of certain monoximes and the structure of the oximes, 2818.
Taylor, *Thomas W. J.*, and *Charles P.* **Woodhouse**, the condensation of quinaldine with *m*-nitrobenzaldehyde, 2971.
Taylor, *William E.* See *John B.* **Shoesmith.**
Tepper, *Wolfe.* See *Frederick M.* **Rowe.**
Terrey, *Henry.* See *Frederick* **Aufenast.**
Thomas, *John S.* See *William* **Pugh.**
Thomason, *Reuben W.* See *Gilbert T.* **Morgan.**
Thornley, *Sidney.* See *Robert* **Robinson.**
Thorpe, (*Sir*) *Edward*, obituary notice of, 1031.
Thorpe, *Jocelyn F.* See *Christopher K.* **Ingold**, *John* **Packer**, and *Eugene* **Rothstein.**
Titley, *Alan F.*, conditions of formation of rings attached to the *o*-, *m*-, and *p*-positions of the benzene nucleus. Part II. The reduction of *m*- and *p*-phenylenediacetonitrile, 508.
Topley, *Bryan.* See *Norman H.* **Chamberlain**, and *John* **Hume.**
Traill, *David.* See *Alexander K.* **Macbeth.**
Trikojus, *Victor M.* See *William H.* **Perkin**, *jun.*
Tucker, *Stanley H.*, iodination in the carbazole series, 546.
the dicarbazyls. Part I. Synthesis of 3:3′-dicarbazyl, 3033.
Turner, *Eustace E.* See *Henry G.* **Dennett**, *Raymond J. W.* **Le Fèvre**, and *Elwyn* **Roberts.**
Turner, *William E. S.*, the physical properties of glasses; the relationship to chemical composition and mode of preparation, 2091.
Tweedy, *Sidney K.* See *James R.* **Partington.**

V.

Venkataraman, *Krishnasami.* See *Robert* **Robinson.**
Verkade, *Pieter E.*, and *Jan* **Coops**, the heat of combustion of salicylic acid, 1437.
Vernon, *William H. J.*, the formation of protective oxide films on copper and brass by exposure to air at various temperatures, 2273.

W.

Wadsworth, *Alan E.*, and *Harry M.* **Dawson**, the systems sodium iodide–acetone and sodium iodide–methyl ethyl ketone, 2784.
Walker, *Oswald J.*, the action of phosphorus on salts of silver and other metals, 1370.
Walker, *Oswald J.* See also *David A.* **Fairweather.**
Walters, *Ernest.* See *Frank* **Briers.**
Ward, *Allan M.*, studies on the Walden inversion. Part X. The reaction between water and the phenylchloroacetate and phenylbromoacetate ions, 1184.
Wardlaw, *William*, and *Arthur J. I.* **Harding**, compounds of tervalent molybdenum. Part IV. Bromides, 1592.
Waters, *William A.* See *Harold A.* **Scarborough.**
Watts, *Harold G.* See *Edmund J.* **Bowen.**
Webb, *Harry W.* See *George A.* **Elliott.**
Werner, *Emil A.*, and *Kenneth C.* **Bailey**, the colour produced by the action of light on concentrated solutions of ammonium thiocyanate, 2970.
West, (*Miss*) *Helen.* See *Robert* **Robinson.**

Westgarth, *George C.* See *Walter N.* **Haworth.**
Wheeler, *Richard V.* See *William R.* **Chapman,** and *Wilfrid* **Francis.**
Whitby, *George S.*, some fatty acid derivatives, 1458.
Whitby, *George S.*, *Jacob* **Dolid,** and *Frederic H.* **Yorston,** the resin of *Hevea* rubber, 1448.
Widdowson, *Ronald R.*, some organosilicon compounds, 958.
Wightman, *Wilfred A.*, the spatial structure of *cyclo*paraffins. Part II. The structure of 1:1-disubstituted *cyclo*hexanes, 2541.
Wignall, *John S.* See *Herbert H.* **Hodgson.**
Wilkins, *Frederick J.* See *George A.* **Elliott.**
Willey, *Eric J. B.*, and *Eric K.* **Rideal,** on active nitrogen. Part I. Its nature and heat of formation, 1804.
Williams, *Leslie T. D.* See *Reginald P.* **Linstead.**
Williams, *Montague.* See *Samuel* **Sugden.**
Willimott, *Stanley G.*, and *Ian A.* **Simpson,** a synthesis of some substituted 3-methylquinolines, 2807.
Wills, *George O.* See *Alexander* **McKenzie.**
Wilson, *Forsyth J.* See *William* **Baird,** and *Herbert N.* **Stephen.**
Wilson, *Ian S.* See *Frank R.* **Goss.**
Wood, *Charles E.*, *John E.* **Such,** and *Frank* **Scarf,** the rotatory dispersion of the esters of lactic acid. Part II. The isomeric butyl esters, 1928.
Wood, *Harold.* See *Harold A.* **Harrison.**
Wood, *John K.* See *James D.* **Mounfield.**
Wood, *Norman E.* See *Francis* **Francis.**
Woodhead, *Donald W.* See *Colin* **Campbell.**
Woodhouse, *Charles P.* See *Thomas W. J.* **Taylor.**
Woodley, *James W.* See *Arthur* **Fairbourne.**
Wright, *Robert*, selective solvent action. Part V. Salting in, 1203.
Wright, (*Miss*) *Winifred M.* See *Eric K.* **Rideal.**

Y.

Yorke, *Albert F.* See *Humphrey R.* **Raikes.**
Yorston, *Frederic H.* See *George S.* **Whitby.**

Z.

Zaki, *Armad.* See *Isidor M.* **Heilbron.**
Zvegintzov, *Michael.* See *Dalziel L.* **Hammick.**

INDEX OF SUBJECTS, 1926.

A.

Acacetin, synthesis of (ROBINSON and VENKATARAMAN), 2344.

Acenaphthpyridine derivatives (NAIR and SIMONSEN), 3140.

β-5-Acenaphthylaminocrotonic acid, ethyl ester and acenaphthylamide of (NAIR and SIMONSEN), 3142.

Acetaldehyde, photolysis of (BOWEN and WATTS), 1607.

Acetanilide *p-di*sulphone and *di*sulphoxides (CHILD and SMILES), 2699.

Acetanilide-*m*-sulphinic acid (CHILD and SMILES), 2699.

Acetanilide-*p*-sulphonyl iodide (CHILD and SMILES), 2701.

Acetic acid, and its ammonium salt, equilibria of water and (SUGDEN), 960.

beryllium salt, conductivity of (SIDGWICK and LEWIS), 2538.

magnesium salt, constitution of aqueous solutions of (RIVETT), 1063.

silver salt, reduction of, by sodium formate (COUTIE), 887.

sodium salt, reactions of, with salts of weak metallic bases (BRITTON), 269.

ethyl ester, effect of various salts and compounds on solubility of (GLASSTONE, DIMOND, and JONES), 2935; (GLASSTONE, DIMOND, and HARRIS), 2939.

Acetic acid, chlorobromo-, optical activity of, and its salts (READ and MCMATH), 2183.

thiol-, ethyl ester, nickel derivative (DRUMMOND and GIBSON), 3076.

Acetic acids, substituted, *sec.*-β-octyl esters, and their rotation (RULE and MITCHELL), 3202.

5-Acetoacetamidoacenaphthene (NAIR and SIMONSEN), 3143.

Acetoacetic acid, ethyl ester, absorption spectra of (MORTON and ROSNEY), 706.

condensation of 3-bromo- and 3-nitro-4-dimethylaminobenzaldehyde with ammonia and (HINKEL and MADEL), 161.

Acetoaceto-α-naphthalide (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2253.

Aceto-*o*-anisidides, nitro- (C. K. and E. H. INGOLD), 1317.

Acetone, photolysis of (BOWEN and WATTS), 607.

catalysis of the reaction between iodine and (DAWSON and CARTER), 2282; (DAWSON and DEAN), 2872.

equilibrium of sodium iodide with (WADSWORTH and DAWSON), 2784.

condensation of β-phenylhydroxylamine and (BANFIELD and KENYON), 1612.

3-phenylthiosemicarbazone (STEPHEN and WILSON), 2534.

semicarbazones (BAIRD and WILSON), 2373.

Aceto-*p*-nitrobenzomethylamide (BRADY and DUNN), 2415.

Aceto-2-nitro-3-methoxy-*p*-toluidide, and its hydrochloride (ROBINSON and SHINODA), 1992.

2-Acetonyl-2-methyl-1:3-benzdithiole (HURTLEY and SMILES), 2267.

Acetophenone semicarbazones (BAIRD and WILSON), 2373.

Acetophenone, ω-amino-, benzoyl derivative, phenylhydrazone (ROBINSON and THORNLEY), 3144.

ω:4-*di*hydroxy-, acetyl derivatives (NOLAN, PRATT, and ROBINSON), 1969.

Acetophenone-*o*-carboxylic acid, menthyl ester (RULE and SMITH), 553.

Aceto-*m*-toluidide, 2:6-*di*chloro-4-nitro-, and its benzoyl derivative, and 2:6-dichloro-4-nitrochloro- (DAVIES and LEEPER) 1416.

3-Acetoxymercuri-5-*iso*amylbenzaldehyde, 2-hydroxy- (HENRY and SHARP), 2438.

2-Acetoxymercuri-*p*-*iso*amylphenol (HENRY and SHARP), 2436.

3-Acetoxymercuri-5-*tert.*-butylbenzaldehyde, 2-hydroxy- (HENRY and SHARP), 2437.

2-Acetoxymercuri-*p*-*tert.*-butylphenol (HENRY and SHARP), 2435.

Acetoxymercuricarvacrol (HENRY and SHARP), 2436.

3-Acetoxymercuri-4-hydroxy-2-methyl-5-*iso*propylbenzaldehyde (HENRY and SHARP), 2439.

5-Acetoxymercuri-3-methyl-6-*iso*propylbenzaldehyde, 4-hydroxy- (HENRY and SHARP), 2439.

Acetylacetone, absorption spectra of (MORTON and ROSNEY), 706.

Acetyl-1:2:3-benztriazole (BELL and KENYON), 954.

Acetyl-*o*-benzylideneaminophenol, and its hydrolysis (BELL and KENYON), 1893.

Acetyl*iso*creosol. See *p*-Tolyl methyl ether, 3-hydroxy-, acetyl derivative.

2-Acetyl-1:2-dihydrobenzthiazole, 5-bromo-1-imino-, and 1-imino-, and its bromides (HUNTER), 1394.

***N*-Acetyldiphenylamine-*p*-arsenious chloride** (BURTON and GIBSON), 461.

Acetylene, absorption of, by colloidal solutions (GATTERER), 299.

δ-Acetylheptoic acid semicarbazone (KON and NUTLAND), 3108.

1-Acetyl*cyclo*hexane-1-acetic acid, and its derivatives (ROTHSTEIN and THORPE), 2016.

1-Acetylisatin, 5-iodo- (AESCHLIMANN), 2910.

2 Acetyl-2-methyl-1:3-benzdithiole (HURTLEY and SMILES), 2267.

Acetylmethylheptoic acids, semicarbazones of (KON and NUTLAND), 3109.

6-Acetyl-9-methyl-ψ-indoxyl*spirocyclo*pentane (MANJUNATH and PLANT), 2263.

Acetyl-*o*-phenylenediamine, preparation of (BELL and KENYON), 954.

Acid, $C_7H_{10}O_4$, and its derivatives, from methylation of ethyl *iso*propylidenemalonate (KON and SPEIGHT), 2730.

$C_9H_{12}O_4$, and its derivatives, from methylation of ethyl *cyclo*pentylidenemalonate (KON and SPEIGHT), 2732.

$C_{10}H_{14}O_4$, and its ester, from methylation of ethyl Δ^1-*cyclo*hexenylmalonate (KON and SPEIGHT), 2734.

$C_{10}H_{16}O_3$, and its cyano-ester, from 2-*iso*propylidene*cyclo*pentanone and ethyl sodiocyanoacetate (KON and NUTLAND), 3108.

$C_{11}H_{18}O_3$, from camphorphorone and ethyl sodiocyanoacetate (KON and NUTLAND), 3109.

Acids, aliphatic, derivatives of (WHITBY), 1453.

fatty, crystal spacing in relation to length of chain in (PIPER, MALKIN, and AUSTIN), 2310.

Acids, fatty *mono*basic, heat of crystallisation of (GARNER, MADDEN, and RUSHBROOKE), 2491.

saturated dicarboxylic, and their ethyl esters, *X*-ray structure of (NORMAND, ROSS, and HENDERSON), 2632.

weak, and their salts, catalysis of the reaction between acetone and iodine by (DAWSON and CARTER), 2282.

Additive reactions and tautomerism (COOPER, C. K. and E. H. INGOLD), 1868.

Address, presidential (CROSSLEY), 978.

Adsorption, optical study of (FODOR and RIWLIN), 102; (RIWLIN), 2300.

Affinity, residual, and co-ordination (MORGAN and SMITH), 912; (MORGAN and BURSTALL), 2018; (MORGAN, CARTER, and HARRISON), 2027.

Air. See Atmospheric air.

Alanine, butyl esters, and their salts (MORGAN), 82.

***dl*-Alanine**, resolution of (KIPPING and POPE), 494.

Alcohol, $C_{28}H_{54}O$, and its acetate, from oxidation of paraffin wax (FRANCIS and GAUNTLETT), 2381.

$C_{28}H_{56}O$, and its acetate, from oxidation of paraffin wax (FRANCIS and GAUNTLETT), 2381.

Alcohols, temperature of maximum density of aqueous mixtures of (MCHUTCHISON), 1898.

of the hydroaromatic and terpene series (GOUGH, HUNTER, and KENYON), 2052.

polyhydric, partial esterification of (FAIRBOURNE and FOSTER), 3146, 3147.

Alcoholates, dissociation pressures of (BONNELL and JONES), 319.

Aldehydes, condensation of piperitone with (EARL and READ), 2072.

Aldehydodiphenyl, 4-hydroxy-, and its phenylhydrazone (BELL and KENYON), 3047.

Aldoximes, isomeric, dissociation constants of (BRADY and GOLDSTEIN), 1918.

methylation of (BRADY and GOLDSTEIN), 2403.

Beckmann rearrangement of *N*-methyl ethers of (BRADY and DUNN), 2411.

Alicyclic compounds, formation and stability of (FARMER and ROSS), 3233.

Aliphatic compounds, higher, synthesis of (G. M. and R. ROBINSON), 2204.

Alkali azides and cyanates, comparison of the physical properties of (CRANSTON and LIVINGSTONE), 501.
bromides, equilibria of ethyl alcohol with (BONNELL and JONES), 318.
Alkaline earth bromides and iodides, equilibria of ethyl alcohol with (BONNELL and JONES), 318.
salts, action of superheated steam on (ROBINSON, SMITH, and BRISCOE), 836.
Alkaloids of the phenanthrene group, syntheses of (ROBINSON and SHINODA), 1987.
Alkyl iodides, reaction of sodium benzyl oxide with (GOLDSWORTHY), 1102.
Alkylation by means of thallium compounds (FEAR and MENZIES), 937.
β-Alkylcinnamic acids, isomerism of (JOHNSON and KON), 2748.
Alkylphenols, and their aldehydes, mercuration of (HENRY and SHARP), 2432.
Allyl esters, oxidation of, to α-glycerides (FAIRBOURNE and FOSTER), 3146.
2:4:6-*tri*nitrophenyl ether (FAIRBOURNE and FOSTER), 3148.
Allyl-Δ¹-*cyclo*hexenylacetone semicarbazone (KON and SMITH), 1797.
Aluminium, periodic passivity of (HEDGES), 2878.
Amidines, tautomerism of (FORSYTH and PYMAN), 2502.
N-alkylated (SEN and RÂY), 646.
Amines, Gabriel synthesis of (ING and MANSKE), 2348.
Amino-acids, butyl esters of (MORGAN), 79.
Amino-alcohols, tertiary, elimination of amino-groups from (MCKENZIE, ROGER, and WILLS), 779.
Amino-compounds, aromatic, Tesla-luminescence spectra of (MCVICKER, MARSH, and STEWART), 17.
Ammonium perhalides, quaternary (READE), 2528.
nitrite, decomposition of aqueous solutions of, by light (HOLMES), 1898.
sulphide, oxidation of (APPLEBEY and LANYON), 2983.
1-Amylaminobenzthiazoles, and their dibromide hydrobromides (HUNTER), 2956.
1-Amylaminobenzthiazoles, 5-bromo-, and their bromides (HUNTER and SOYKA), 2963.
2-Amylamino-β-naphthathiazoles, and their bromides (DYSON, HUNTER, and SOYKA), 2968.
5-*iso*Amylbenzaldehyde, 2-hydroxy-, and its derivatives (HENRY and SHARP), 2437.
Analysis, microchemical (HARTUNG), 840.
Anhydro-5-amino 2-βββ-*tri*chloro-α-hydroxyethoxy-1-βββ-*tri*chloro-α-hydroxyethylbenzene, and its derivatives (CHATTAWAY), 2725.
Anhydro-2-βββ-*tri*chloro-α-hydroxyethoxy-1-βββ-*tri*chloro-α-hydroxyethylbenzene (CHATTAWAY), 2726.
Anhydrocotarnine-2:4-*di*aminotoluene, and its diacetyl derivative (ROBINSON and WEST), 1985.
Anhydrocotarnine-2-nitro-4-amino-3-methoxytoluene, and its acetyl derivative (ROBINSON and SHINODA), 1991.
Anhydrocotarnine-2:6-*di*nitrohomoveratrole (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1976.
Anhydrocotarnine-2:4-*di*nitro-3-methoxytoluene, and its hydrochloride (ROBINSON and WEST), 1986.
Anhydrodihydrocryptopine oxide, and its hydrochloride (HAWORTH and PERKIN), 1779.
Anhydrodihydroprotopine, and its oxide (HAWORTH and PERKIN), 1782.
Anhydrohydrastinine-2:4:6-*tri*nitrotoluene, and its hydrochloride (ROBINSON and WEST), 1987.
Anhydrolaudaline-2:4-*di*amino-3-methoxytoluene, and its dihydrochloride and acetyl derivative (ROBINSON and SHINODA), 1990.
Anhydrolaudaline-2-nitro-4-amino-3-methoxytoluene, and its derivatives (ROBINSON and SHINODA), 1990.
Anhydrolaudaline-2:4-*di*nitro-3-methoxytoluene, and its hydrochloride (ROBINSON and SHINODA), 1990.
Anhydro-5-nitro-2-βββ-*tri*chloro-α-hydroxyethoxy-1-βββ-*tri*chloro-α-hydroxyethylbenzene (CHATTAWAY), 2722.
Anhydrotetrahydromethylberberine oxide, and its hydrochloride (HAWORTH and PERKIN), 449.
Aniline, chloro-derivatives, preparation of (DYSON, GEORGE, and HUNTER), 3043.
Anilines, chloro-substituted, action of thiocarbonyl chloride on (DYSON, GEORGE, and HUNTER), 3041.
4'-Anilinodiphenyl, bromo- and chloro-*di*nitro- (LE FÈVRE and TURNER), 2047.
β-Anilino β-methylpentan-δ-one, **β-*p*-**chloro-, and its derivatives (BANFIELD and KENYON), 1623.

4-Anilino-2-phenyldimethylpyrimidinium salts (FORSYTH and PYMAN), 2508.

***o*-Anisidine**, 3- and 6-nitro- (C. K. and E. H. INGOLD), 1318.

Anisidines, chloro- (HODGSON and HANDLEY), 542.

Anisidine methyl thioethers, and their hydrochlorides (HODGSON and HANDLEY), 544.

Anisole, *o*-fluoro-, and its nitro-derivatives (HOLMES and INGOLD), 1329.

5-halogeno-3-hydroxy-derivatives, and their derivatives (HODGSON and WIGNALL), 2826.

Anisole-2-sulphinic acids, nitro- (HOLMES, C. K. and E. H. INGOLD), 1688.

ω-Anisoyl-3:4-dimethoxyacetophenone (BRADLEY and ROBINSON), 2366.

α-Anisoylpropiophenone, and its copper derivative (BRADLEY and ROBINSON), 2360.

Anisylidene-*dl*-piperitone (EARL and READ), 2073.

***p*-Anisyltelluri*tri*chloride** (MORGAN and KELLETT), 1084.

Annual General Meeting, 962.

Anodes, deposition of zinc on, in voltaic cells (HUMBY and PERRIN), 959.

cadmium, lead, magnesium, mercury, platinum, tin, and zinc, periodic phenomena at (HEDGES), 2581.

copper and silver, periodic phenomena at (HEDGES), 1533.

Anthocyanins, synthesis of (ROBERTSON and ROBINSON), 1713.

Anthracene, and its derivatives, absorption spectra of (CAPPER and MARSH), 724.

Anthracenes, *meso*-substituted (INGOLD and MARSHALL), 3080.

reactivity of (COOK), 1282, 1677, 2160.

Anthragallol, acetyl derivatives (GREEN), 2202.

9-Anthranyl acetates, 1- and 4-chloro- (MATTHEWS), 241.

Anthranyl-9-pyridinium chloride, 10-hydroxy- (MATTHEWS), 243.

Anthraphenone, 10-bromo-, -chloro-, and -nitro- (COOK), 1285.

Anthrapurpurin, acetyl and benzoyl derivatives (GREEN), 2200.

Anthraquinone, 1-chloro-4-hydroxy-, and its 4-acetyl derivative (GREEN), 1434.

5-chloro-1-hydroxy-, and its acetyl derivative (GREEN), 2199, 2203.

10-chloro-1-hydroxy-, and its derivatives (GREEN) 1431.

Anthraquinones, hydroxy-, action of thionyl chloride on (GREEN), 1428, 2198.

Anthrone, 10-*mono*- and 4:10-*di*-chloro-, chlorobromo-, and chlorohydroxy- (MATTHEWS), 241.

***meso*Anthrones**, hydroxy-, reactions of (MATTHEWS), 236.

Antimony *tri*chloride, action of, on diazotised diamines (GRAY), 3174.

***d*-Arabinose**, oxidation of (MCOWAN), 1747.

Aromatic compounds, substitution in (DAVIES and LEEPER), 1413; (FLÜRSCHEIM and HOLMES), 1562.

directive power of groups in substitution in (ALLAN and ROBINSON), 376; (OXFORD and ROBINSON), 383; (ROBINSON and SMITH), 392; (ALLAN, OXFORD, ROBINSON, and SMITH), 401; (LEA and ROBINSON), 411; (HOLMES, C. K. and E. H. INGOLD), 1684.

mercuration of (COFFEY), 637, 3215.

introduction of selenocyano-groups into (CHALLENGER, PETERS, and HALÉVY), 1648.

polynuclear, molecular configuration of (CHRISTIE and KENNER), 470; (CHRISTIE, HOLDERNESS, and KENNER), 671.

Arsenic compounds, reduction of, by sodium hyposulphite (FARMER and FIRTH), 119.

Arsenites, action of, on halogenated organic compounds (BALABAN), 569.

Arsenic *sub*sulphide (FARMER and FIRTH), 119.

Arsenobenzene, 4-amino-, 3′-aminobenzene- and -toluene-sulphonyl derivatives (HEWITT, KING, and MURCH), 1362.

5:5′-*di*iodo-3:3′-*di*amino-4:4′-*di*hydroxy-, diacetyl derivative, and 5:5′-*di*iodo-3:3′-*di*nitro-4:4′-*di*hydroxy- (MACALLUM), 1646.

thiol- (HEWITT, KING, and MURCH), 1370.

Arsenobenzenes, aminohydroxy-, aminoaryl derivatives of (HEWITT and KING), 827.

Aryl alkyl ethers, reactions of tellurium tetrachloride and (MORGAN and KELLETT), 1080.

*di*sulphoxides, amino-, phototropic (CHILD and SMILES), 2696.

Arylsulphuric acids (BURKHARDT and LAPWORTH), 684.

Atmospheric air, propagation of flame in mixtures of methane and (CHAPMAN and WHEELER), 2139.

Atomic weight of boron (BRISCOE, ROBINSON, and STEPHENSON), 70.
of silicon (ROBINSON and SMITH), 1262.
of silver (RILEY and BAKER), 2510.
Aurous oxide. See under Gold.
Azelaic acid, *aa'-di*hydroxy-, and its silver salt and ethyl ester (GOSS and INGOLD), 1476.
Azides, comparison of the physical properties of cyanates and (CRANSTON and LIVINGSTONE), 501.
Azobenzaldehydes, preparation of (DUTT), 1172.
Azobenzthiazole, 1-amino-, and its hydrochloride (HUNTER), 1396.
Azodicarboxymethylamide (COOPER and INGOLD), 1895.
p-**Azoxybenzyl alcohol** (SHOESMITH and TAYLOR), 2834.
Azoxybenzyl bromides, isomeric, preparation and hydrolysis of (SHOESMITH and TAYLOR), 2832.

B.

Balance, micro-. See Micro-balance.
Balance sheets of the Chemical Society and Research Fund. See Annual General Meeting, 962.
Barbituric acid, bromo- and chloro-, hydrazides of (MACBETH, NUNAN, and TRAILL), 1251.
Barium chloride and nitrate, equilibria of sodium chloride and nitrate with (FINDLAY and CRUICKSHANK), 316.
germanate (PUGH), 2831.
iodide, solubility of, in water (PACKER and RIVETT), 1061.
Base, $C_{12}H_{19}ON$, and its derivatives, from reduction of $C_{18}H_{22}O_2N_2$ (BANFIELD and KENYON), 1628.
Bases, heterocyclic, reactive methyl groups in (HUMPHRIES), 374.
organic, action of acetylene tetrabromide on (FULTON), 197.
Benzaldehyde, 2-chloro-5-amino-, and chloro-*m*-hydroxy-derivatives, and their derivatives (HODGSON and BEARD), 147.
chloronitro-3-hydroxy-derivatives, and their salts and derivatives (HODGSON and BEARD), 2031.
m-nitro-, condensation of quinaldine with (TAYLOR and WOODHOUSE), 2971.
Benzaldehydes, chloro-3-hydroxy-, nitration of (HODGSON and BEARD), 2030.
fluoro-, and their derivatives (SHOESMITH, SOSSON, and SLATER), 2760.
Benzamidines, nitration of (FORSYTH, NIMKAR, and PYMAN), 800.
1:4-Benzdithian-2:3-dione (HURTLEY and SMILES), 2268.
1:3-Benzdithiole, 2-oximino-, and 2-thio- (HURTLEY and SMILES), 1826.
1:3-Benzdithiol-2-one, and nitro- (HURTLEY and SMILES), 1826.
1:3-Benzdithiylium salts (HURTLEY and SMILES), 2267.
Benzene nucleus, structure of (INGOLD and MARSHALL), 3080.
formation of rings attached to (TITLEY), 508.
vapour pressure of (JOLLY and BRISCOE), 2156.
derivatives, vicinal trisubstituted, substitution in (RUBENSTEIN), 648.
Benzene, chloronitro-, action of alcoholic potassium hydroxide on (RICHARDSON), 522.
*o-di*thiol- (HURTLEY and SMILES), 1821.
p-**Benzeneazo**-*p'p''-di*aminotriphenylmethane, and *p*-4-hydroxy- (DUTT), 1175.
Benzeneazobenzeneazobenzeneazoaniline (DUTT), 1177.
Benzeneazobenzeneazobenzeneazobenzeneazodimethylaniline (DUTT), 1178.
Benzeneazobenzeneazobenzeneazobenzeneazophenol (DUTT), 1178.
Benzeneazobenzeneazobenzeneazodimethylaniline (DUTT), 1177.
Benzeneazobenzeneazobenzeneazophenol (DUTT), 1177.
Benzene-1-azo-β-napthaquinone-1-sulphonic acid, 4'-nitro-, sodium salt (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 699.
Benzenediazonium chloride, *p*-amino-, acetyl derivative, and its derivatives (GRAY), 3178.
Benzene-*o*-dimethylsulphone (HURTLEY and SMILES), 1825.
Benzene-*o*-disulphonic acid, salts and derivatives of (HURTLEY and SMILES), 1823.
Benzenesulphonic acid, beryllium salt (SIDGWICK and LEWIS), 1290.
Benzenesulphonic acid, *p*-amino-, acetyl derivative, *p*-acetylaminophenyl ester (CHILD and SMILES), 2699.
Benzenethiolsulphonic acid, *p*-amino-, acetyl derivative, *p*-tolyl ester (CHILD and SMILES), 2702.
Benzenyltrimethylamidine nitrate, and *m*-nitro-, hydriodide (FORSYTH, NIMKAR and PYMAN), 803.
Benzfuroin (GREENE), 331.

Benzidines, *di*nitro-, and their diacetyl and dipiperidino-derivatives (LE FÈVRE and TURNER), 1762.
Benzil, *oo'*-, *om'*-, and *mm'*-*di*nitro- (CHATTAWAY and COULSON), 1070.
2:4-*di*nitro-, oximes (BISHOP and BRADY), 810.
3:5:3':5'-*tetra*nitro-, and its quinoxaline derivative (CHRISTIE and KENNER), 475.
Benziminazole-2-thioglycollic acid, esters and lactam (STEPHEN and WILSON), 2536.
Benzoic acid, ethyl ester, chloro- and methoxy-derivatives, velocity of saponification of (BLAKEY, MCCOMBIE, and SCARBOROUGH), 2863.
Benzoic acid, 3-amino-4-hydroxy-, *N*-4-toluenesulphonyl derivative (HEWITT, KING, and MURCH), 1368.
3-bromo-2-amino-, acetyl derivative (BURTON, HAMMOND, and KENNER), 1803.
3-bromonitro-, ethyl ester (BURTON, HAMMOND, and KENNER), 1804.
p-nitro-, and 3:5-*di*nitro-, allyl esters and their dibromo-derivatives (FAIRBOURNE and FOSTER), 3147.
Benzoic acids, nitro-, *sec.*-β-octyl esters of, and their rotation (RULE and NUMBERS), 2116.
Benzomethylamide, *o*-nitro- (BRADY and DUNN), 2415.
Benzophenones, hydroxy-, preparation of (ATKINSON and HEILBRON), 2688.
methoxylated, fission of (LEA and ROBINSON), 2351.
Benzopyrylium salts, synthesis of (PERKIN, RÂY, and ROBINSON), 941.
Benzoxazole methiodide (CLARK), 233.
ω-Benzoylacetophenones, chloro- and nitro-, and their copper derivatives (BRADLEY and ROBINSON), 2363.
α-Benzoylcamphor, absorption spectra of (MORTON and ROSNEY), 708.
Benzoyldi-*p*-tolylamine, thio- (CHAPMAN), 2298.
Benzoylfurfuraldehydecyanohydrin (GREENE), 330.
Benzoylfuroin (GREENE), 331.
***o*-Benzoylmethylaminoanisole** (CLARK), 235.
***o*-Benzoylmethylaminophenylurethane** (CLARK), 235.
ω-Benzoyloxyphloracetophenone, and its triacetyl derivative (HEAP and ROBINSON), 2340.
ω-Benzoyloxyresacetophenone, and its diacetyl derivative (HEAP and ROBINSON), 2338.
2-Benzoyl-2-phenyl-1:3-benzdithiole (HURTLEY and SMILES), 2267.
2-Benzoyl-2-phenyl-1:3-dithiolan (HURTLEY and SMILES), 2267.
Benzoylvanillic acid, and its derivatives (HEAP and ROBINSON), 2341.
Benzthiazole, 1-amino-, acetyl and benzoyl derivatives, and their bromides (HUNTER), 1395.
amino- and bromoamino-derivatives, and their derivatives (HUNTER), 1397.
Benzthiazoles, amino- (HUNTER), 1385, 1401, 2951; (HUNTER and SOYKA), 2958; (DYSON, HUNTER, and SOYKA), 2964.
Benzthiazole-1-azo-β-naphthol (HUNTER), 1396.
Benzyl bromides, bromo-, chloro-, and fluoro- (SHOESMITH and SLATER), 214.
iodides, bromo- (SHOESMITH and SLATER), 219.
Benzylacetone, δ-anilino- and δ-methylanilino-semicarbazones and *p*-tolylhydrazone (BAIRD and WILSON), 2373.
Benzylamine, nitration of, and its derivatives (ING and ROBINSON), 1655; (GOSS, INGOLD, and WILSON), 2440.
3-Benzylaminotoluene, 2:4-*di*nitro- (GORNALL and ROBINSON), 1984.
Benzylammonium picrates, nitro- (GOSS, INGOLD, and WILSON), 2455.
9-Benzylanthracene, bromo-derivatives, and 10-chloro- and 10-nitro- (COOK), 2166.
9-Benzylanthranyl 10-acetate (COOK), 2165.
9-Benzylanthranyl-10-pyridinium bromide (COOK), 2167.
10-Benzylanthraphenone (COOK), 2169.
***d*- and *l*-Benzyldeoxybenzoin** (MCKENZIE, ROGER, and WILLS), 788.
9-Benzyl 9:10-dihydroanthracene, 9-hydroxy-10-nitro- (COOK), 2168.
10-Benzyl-9:10-dihydroanthraphenone (COOK), 2170.
9-Benzyl-9:10-dihydroanthraquinyl-9:10-dipyridinium *di*bromide (COOK), 2167.
Benzyldiethylamine, nitration of (FLÜRSCHEIM and HOLMES), 1567.
Benzyldimethylamine, *m*-nitro- (GOSS, INGOLD, and WILSON), 2454.
Benzyldimethylarsine, derivatives of (ROBERTS, TURNER, and BURY), 1445.
Benzylethyldibutylstannane (LAW), 3243.
Benzylideneacetyl*iso*propylidenebenzidine, *p*-nitro- (DENNETT and TURNER), 481.
4-Benzylideneaminodiphenyl (BELL and KENYON), 2707.

4-Benzylideneamino-4′-hydroxydiphenyl (BELL and KENYON), 2712.
Benzylideneanthrone *di*bromide (COOK), 2171.
Benzylidenesalicylidenebenzidine, *p*-nitro- (DENNETT and TURNER), 481.
Benzyl methyl ketone, condensation of, with salicylaldehyde (DICKINSON), 2234.
Benzyl oxide, sodium, reactions of, with alkyl iodides (GOLDSWORTHY), 1102.
2-Benzyloxyanisole, nitro-derivatives (ALLAN and ROBINSON), 382; (OXFORD and ROBINSON), 386.
4-Benzyloxyanisole, nitro-derivatives (ROBINSON and SMITH), 399.
10-Benzyloxy-5:10-dihydrophenarsazine (BURTON and GIBSON), 464.
4-Benzyl-2-pyridone, 3:5-*di*cyano-6-hydroxy-, and its ammonium salt (LINSTEAD and WILLIAMS), 2747.
1-Benzyltetrahydro*iso*quinoline, derivatives of (ROBINSON and WEST), 1985.
Benzyltriethylammonium picrate, and nitro-derivatives (GOSS, INGOLD, and WILSON), 2450.
Benzyltrimethylammonium salts, and nitro- (ING and ROBINSON), 1666.
Berberine, conversion of, into β-homochelidonine (HAWORTH and PERKIN), 445.
Beryllium compounds, co-ordination, optical activity of (MILLS and GOTTS), 3121.
Beryllium oxide, solubility of, in solutions of its salts (SIDGWICK and LEWIS), 1287.
Beryllium organic compounds:—
salts, conductivities of (SIDGWICK and LEWIS), 2538.
Berylliobenzoylpyruvic acid, salts of, and their resolution (MILLS and GOTTS), 3126.
Bis*tri*aminopropanecobaltic salts (MANN and POPE), 2678.
Bis*tri*aminopropanecupric salts (MANN), 2686.
Bis*tri*aminopropanenickelous salts (MANN and POPE), 2680.
Bis-*p*-anisyl tellurides (MORGAN and KELLETT), 1084, 1085.
2:2′-Bis-1:3-benzdithiolene, and *tetra*-iodo- (HURTLEY and SMILES), 2263.
2:2′-Bis-1:3-benzdithiylium sulphate (HURTLEY and SMILES), 2269.
Bis-2:5-*di*chlorophenylthiolphenylacetic acid, ethyl ester, and nitrile (BROOKER and SMILES), 1726.
Bis-dibenzyl ketone thiocarbohydrazone (STEPHEN and WILSON), 2537.
10:10′-Bis-5:10-dihydrophenarsazine, and its acetyl derivative (BURTON and GIBSON), 2246.
Bis-*p*-dimethylaminobenzylidene pentaerythritol methiodide (FAIRBOURNE and WOODLEY), 3241.
Bisdiphenylene-ethylene, absorption spectrum of (CAPPER and MARSH), 725.
Bisethylenediamminocupric iodides, mono- and di-hydrated, thermal properties of (MORGAN, CARTER, and HARRISON), 2030.
Bismethanolbisethylenediamminocupric cyanate tetrahydrate (MORGAN and BURSTALL), 2027.
Bis-2-methoxy-*m*-tolyl *di*telluride (MORGAN and KELLETT), 1086.
2:3 9:10-Bismethylenedioxyanhydroprotoberberine-acetone (HAWORTH and PERKIN), 1784.
2:3:9:10-Bismethylenedioxydihydroprotoberberine, and its hydrochloride (HAWORTH and PERKIN), 1783.
2:3:9:10-Bismethylenedioxyoxyprotoberberine (HAWORTH and PERKIN), 1780.
2:3:9:10-Bismethylenedioxyprotoberberinium chloride (HAWORTH and PERKIN), 1783.
2:3:9:10-Bismethylenedioxytetrahydroprotoberberine, and its hydrochloride (HAWORTH and PERKIN), 1780.
Bistetramethyl*di*aminodiphenylcarbinol *di*acetate (DUTT), 1178.
Bistetramethyl*di*aminodiphenylmethane (DUTT), 1178.
Boiling points of higher aliphatic hydrocarbons (FRANCIS and WOOD), 1420.
Boron, atomic weight of (BRISCOE, ROBINSON, and STEPHENSON), 70.
*tri*oxide glass, density of (BRISCOE, ROBINSON, and STEPHENSON), 70.
Boric acid, fractional crystallisation of, and the density of boric oxide therefrom (BRISCOE, ROBINSON, and STEPHENSON), 954.
Borates, basic, electrometric precipitation of (BRITTON), 136.
Brass, formation of oxide films on (VERNON), 2273.
Brazilin, synthesis of, and its derivatives (PERKIN, RÂY, and ROBINSON), 941.
Bromine, light absorption of wet and dry (LEWIS and RIDEAL), 596.
Budde effect in (LEWIS and RIDEAL), 583, 596.
wet, photoactive constituent of (LEWIS and RIDEAL), 583.
vapour pressure of (JOLLY and BRISCOE), 2158.

Bromine, reaction of ethylene with (NORRISH and JONES), 55.
Budde effect in bromine (LEWIS and RIDEAL), 583, 596.
Butane-$\alpha\alpha\beta\gamma$-tetracarboxyamide (INGOLD and SHOPPEE), 1917.
Butenylnaphthalenes, γ-oximino- (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2258.
2-Butoxyanisoles, nitro-derivatives (ALLAN and ROBINSON), 381.
10-*n*-Butoxy-5:10-dihydrophenarsazine (BURTON and GIBSON), 464.
1-Butylaminobenzthiazoles, and their bromides (HUNTER), 2955.
1-Butylaminobenzthiazoles, 5-bromo-, and their dibromides (HUNTER and SOYKA), 2962.
2-Butylamino-β-naphthathiazoles, and their bromides (DYSON, HUNTER, and SOYKA), 2967.
5-*tert.*-Butylbenzaldehyde, 2-hydroxy-, phenylhydrazone (HENRY and SHARP), 2437.
***d*-*sec.*-Butylbenzene**, preparation and rotation of, and its derivatives (HARRISON, KENYON, and SHEPHERD), 658.
Butyl-Δ^1-*cyclo*hexenylacetone semicarbazone (KON and SMITH), 1797.
***sec.*-Butyl*iso*valerylacetic acid**, ethyl ester (JONES), 2769.
Butyrylcarbamide, α-bromo- (PHILLIPS), 2981.

C.

Cade oil, sesquiterpene from (HENDERSON and ROBERTSON), 2813.
Cadinene, chemistry of (HENDERSON and ROBERTSON), 2811.
action of chromic acid and of chromyl chloride on (GIBSON, ROBERTSON, and SWORD), 166.
Cadmium sulphide, precipitation of, in presence of hydrochloric acid and chlorides (KRISHNAMURTI), 1549.
Cadmium anodes. See under Anodes.
Calcium carbonate hexahydrate, density of (HUME and TOPLEY), 2932.
sulphate, precipitated (LAMBERT and SCHAFFER), 2648.
Camphane series, studies in (FORSTER and RAO), 2670.
Camphor, absorption spectra of halogen and sulphonic derivatives of (LOWRY and OWEN), 606.
Camphor, *iso*nitroso-, unstable form of (FORSTER and RAO), 2670.
thiol-, metallic derivatives of (DRUMMOND and GIBSON), 3075.
Camphor series, melting-point curves of isomerides in (ROSS and SOMERVILLE), 2770.
***d*-Camphoramic acid**, rotation of aryl derivatives of (SINGH and PURI), 504.
***d*-Camphorimide**, rotation of aryl derivatives of (SINGH and PURI), 504.
Caoutchouc, from *Hevea brasiliensis*, resin of (WHITBY, DOLID, and YORSTON), 1448.
Carbamidoacetic acid, *n*-butyl ester (MORGAN), 81.
Carbamyl chlorides, substituted, decomposition of, by hydroxy-compounds (PRICE), 653, 3230.
Carbamyl*cyclo*hexanecarboxylic acids, and their esters (WIGHTMAN), 2543.
Carbazole, 3-*mono*- and 3:6-*di*-iodo-, and their 9-acetyl, 9-benzoyl, and 9-toluene-*p*-sulphonyl derivatives (TUCKER), 547.
Carbazoles, synthesis of (OAKESHOTT and PLANT), 1210.
Carbazole series, iodination in (TUCKER), 546.
δ-Carbethoxyanilinosemicarbazide hydrochloride, and its benzylidene derivative (BAIRD and WILSON), 2375.
3-*o*-Carbethoxybenzylacetylacetone, and its copper derivative (MORGAN and PORTER), 1262.
3-*m*-Carbethoxybenzylacetylacetone, and its copper derivative (MORGAN and PORTER), 1258.
3-*m*-Carbethoxybenzylbutyrylacetone, and its copper derivative (MORGAN and PORTER), 1260.
ω-4-Carbethoxy-2-keto*cyclo*pentylmethylsuccinic acid, ethyl ester, and its semicarbazone (INGOLD and SHOPPEE), 1917.
2-Carbethoxy-7-methoxyindole-3-acetic acid, ethyl ester (PERKIN and RUBENSTEIN), 362.
Carbon chains, alternating effect in (HOLMES and INGOLD), 1305, 1328; (C. K. and E. H. INGOLD), 1310; (HOLMES, C. K. and E. H. INGOLD), 1684; (GOSS, INGOLD, and WILSON), 2440; (BAKER and INGOLD), 2462.
rings, influence of, on the velocity of reactions involving side-chains (GANE and INGOLD), 10.
Carbon *mon*oxide, catalytic dissociation of (CLEMINSON and BRISCOE), 2148.
ignition of mixtures of hydrogen and (CAMPBELL and WOODHEAD), 3010.
***di*oxide**, absorption of, by colloidal solutions (GATTERER), 299.
Carbonates, basic, electrometric precipitation of (BRITTON), 142.

Carbon *di*sulphide, flame spectra of (EMELÉUS), 2948.
Carbonylbenzidine, and its derivatives (LE FÈVRE and TURNER), 2483.
3-*m*-Carboxybenzylacetone (MORGAN and PORTER), 1261.
3-*m*-Carboxybenzylacetylacetone, and its copper derivatives (MORGAN and PORTER), 1259.
3-*m*-Carboxybenzylbutyrylacetone, and its beryllium and copper derivatives (MORGAN and PORTER), 1260.
***o*-Carboxycinnamonitrile** (EDWARDS), 816.
β-(2-Carboxydimethoxyphenyl)ethylamines, β-hydroxy-, and their lactones, salts and derivatives of (EDWARDS), 745.
β-(2-Carboxydimethoxyphenyl)ethylcarbamic acids, β-hydroxy-, ethyl ester, lactones (EDWARDS), 746.
β-(2-Carboxydimethoxyphenyl)ethylmethylamines, β-hydroxy-, and their lactones, salts and derivatives of (EDWARDS), 747.
1-Carboxy*cyclo*hexane-1-acetic acid, preparation of, and its anhydride (ROTHSTEIN and THORPE), 2015.
***cis-o*-Carboxy*cyclo*hexaneacetic acid**, preparation of (KON and QUDRAT-I-KHUDA), 3071.
***o*-Carboxy-α-hydroxycinnamic acid** *p*-nitrophenylhydrazide (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 705.
β-(2-Carboxy-3:4-*di*hydroxyphenyl) ethylamine, β-hydroxy-, and its hydrochloride (EDWARDS), 746.
α- and ω-4-Carboxy-2-keto*cyclo*pentylmethylsuccinic acids (INGOLD and SHOPPEE), 1916.
2-Carboxy-5- and -7-methoxyindole-3-acetic acids (PERKIN and RUBENSTEIN), 361.
***m*-Carboxyphenyl** methyl sulphoxide, preparation and resolution of (HARRISON, KENYON, and PHILLIPS), 2087.
***o*-Carboxyphenylethylamines**, substituted (EDWARDS), 740.
***m*-Carboxyphenylsulphuric acid**, potassium salt (BURKHARDT and LAPWORTH), 689.
Carone, catalytic hydrogenation of (IYER and SIMONSEN), 2049.
β-Caryophyllene, action of chromyl chloride on (GIBSON, ROBERTSON, and SWORD), 165.
Caryophyllene series (HENDERSON, ROBERTSON, and KERR), 62.
Caryophyllene alcohol (HENDERSON, ROBERTSON, and KERR), 66.
Caryophyllene glycol (HENDERSON, ROBERTSON, and KERR), 68.
Caryophyllol, and its dibromide (HENDERSON, ROBERTSON, and KERR), 65.
Catalytic reactions, acid and salt effects in (DAWSON and CARTER), 2282; (DAWSON and DEAN), 2872; (DAWSON and HOSKINS), 3166.
Catechol. See Pyrocatechol.
Cedrene, action of chromyl chloride on (GIBSON, ROBERTSON, and SWORD), 166.
Cells, electrochemical, alternating-current (HEDGES), 1892.
Cellulose, degradation of (IRVINE and ROBERTSON), 1488.
Charcoal, low temperature oxidation with (RIDEAL and WRIGHT), 1813, 3182.
blood, catalytic activity of (RIDEAL and WRIGHT), 3182.
Chemical constitution. See under Constitution.
Chloral, condensation of phenols with (CHATTAWAY), 2720.
Chloral hydrate, effect of heat on (MOUNFIELD and WOOD), 498.
Chlorine *di*oxide, vapour pressure of (KING and PARTINGTON), 925.
Chloroauric acid. See under Gold.
Chromium, removal of, from amalgams (RUSSELL, EVANS, and ROWELL), 1872.
Chromium salts, reactions of, with sodium acetate, oxalate, and tartrate (BRITTON), 269.
Chromic chloride hexahydrates, miscibility of dilute solutions of (HOWARD and PATTERSON), 2791.
nitrate hydrates (PARTINGTON and TWEEDY), 1142.
Chromyl chloride, oxidation of sesquiterpenes by (GIBSON, ROBERTSON, and SWORD), 164.
Chromic acid, oxidation of sesquiterpenes by (GIBSON, ROBERTSON, and SWORD), 164.
Chromates, basic, electrometric precipitation of (BRITTON), 125.
Chrysin, synthesis of (ROBINSON and VENKATARAMAN), 2347.
Chrysogen, absorption spectrum of (CAPPER and MARSH), 725.
***allo*Cinnamic acid**, *o*-cyano-, preparation of (EDWARDS), 815.
Cinnamic acids, and their amides, substituted derivatives of (HARRISON and WOOD), 1195.
7-Cinnamoyloxy-4′-methoxy-2-styryl-*iso*flavone, 5-hydroxy- (BAKER and ROBINSON), 2718.
Citraconic acid, ethyl ester, action of ethyl sodiomalonate on (INGOLD and SHOPPEE), 1912.
Coal, composition of (FRANCIS and WHEELER), 1410.

Cobalt, electro-deposition potential of (GLASSTONE), 2887.
periodic passivity of (HEDGES), 2878.
removal of, from amalgams (RUSSELL, EVANS, and ROWELL), 1872.
Cobalt alloys with iron and nickel, electro-deposition potentials of (GLASSTONE), 2897.
Cobalt *per*oxide as catalyst (CHIRNOAGA), 1695.
Cobalt organic compounds, complex, with oximes (TAYLOR and EWBANK), 2818.
Codeine, oxidation of (CAHN and ROBINSON), 908.
Colloids, protective (SUGDEN and WILLIAMS), 2424.
Colloidal solutions, absorption of gases by (GATTERER), 299.
Colour, theory of (DUTT), 1171.
and constitution (HODGSON and HANDLEY), 542.
Colouring matters. See Hæmoglobin.
Compounds, conjugated, properties of (FARMER and ROSS), 1570.
sparingly soluble, determination of solubility of (MITCHELL), 1333.
spiro-**Compounds**, formation and stability of (ROTHSTEIN and THORPE), 2011.
Conessine, and its derivatives (KANGA, AYYAR, and SIMONSEN), 2123.
*apo***Conessine**, and its salts (KANGA, AYYAR, and SIMONSEN), 2125.
Constitution, chemical, and optical rotatory power (SINGH and PURI), 504; (HARRISON, KENYON, and SHEPHERD), 658; (DOMLEO and KENYON), 1841; (HARRISON, KENYON, and PHILLIPS), 2079.
and colour (HODGSON and HANDLEY), 542.
and trypanocidal action (HEWITT and KING), 817; (HEWITT, KING, and MURCH), 1355.
Co-ordination and residual affinity (MORGAN and SMITH), 912; (MORGAN and BURSTALL), 2018; (MORGAN, CARTER, and HARRISON), 2027.
Copaene, new source of (HENDERSON, M'NAB, and ROBERTSON), 3077.
Copper, formation of oxide films on (VERNON), 2273.
action of sulphuric acid on (ROGERS), 254.
Copper compounds, co-ordination, optical activity of (MILLS and GOTTS), 3121.
Copper hydrides, and their crystal structure (MÜLLER and BRADLEY), 1669.
sulphates, basic (FOWLES), 1845; (BRITTON), 2868.
Copper organic compounds:—
with ethylenediamine (MORGAN and BURSTALL), 2018.
complex, with oximes (TAYLOR and EWBANK), 2818.
Cupric compounds with ethylenediaminobisacetylacetone (MORGAN and SMITH), 918.
Copper anodes. See under Anodes.
Corrosion, liquid-line (HEDGES), 831.
Cosmetic, Egyptian, from the tomb of Tu'-ankh-Amen (CHAPMAN and PLENDERLEITH), 2614.
*iso***Creosol**, and *di*nitro-, and their salts and derivatives (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1972.
2-nitro-6-amino-, and its acetyl derivative (GULLAND and ROBINSON), 1979.
m-**Cresol**, chloro-derivatives, and their derivatives (GIBSON), 1424.
Cresols, halogen derivatives, and their amino- and nitroso-derivatives (HODGSON and MOORE), 2036.
Crotonic acid series (PHILLIPS), 2979.
Crotonylcarbamides (PHILLIPS), 2981.
Cryptopine, synthesis of (HAWORTH and PERKIN), 1769.
*α-allo***Cryptopine.** See β-Homochelidonine.
Crystals, structure of, in relation to length of chain in organic compounds (PIPER, MALKIN, and AUSTIN), 2310.
variation of angles of, during growth (HEDGES), 791.
Cubebol, and its derivatives (HENDERSON and ROBERTSON), 2815.
Cupribenzoylpyruvic acid, strychnine salt (MILLS and GOTTS), 3130.
Cyanogen:—
Hydrocyanic acid, specific heat of (INGOLD), 26, 2816; (PARTINGTON), 1559.
potassium salt, equilibria of formation of double salts of, with cadmium, mercury, nickel, and zinc cyanides (CORBET), 3190.
Cyanates, comparison of the physical properties of azides and (CRANSTON and LIVINGSTONE), 501.
Cyclic compounds, formation of, from halogenated open-chain derivatives (HASSELL and INGOLD), 1465; (GOSS and INGOLD), 1471.

D.

Decahydro-β-naphthamides (KAY and STUART), 3038.

Dehydro-anhydrolaudaline-4-amino-3-methoxytoluene, 4-acetyl derivative, methiodide (ROBINSON and SHINODA), 1994.

Delphinidin chloride 3-methyl ether (GATEWOOD and ROBINSON), 1959.

Deoxytetrahydro-α-methylmorphimethine *per*chlorate (CAHN), 2565.

Dextrose, structure of (CHARLTON, HAWORTH, and PEAT), 89; (HIRST), 350.

action of, on zirconium chloride solutions (BRITTON), 269.

***s*-Di-5-acenaphthylcarbamide** (NAIR and SIMONSEN), 3143.

Diacetophenonethiocarbohydrazone, sodium derivative (STEPHEN and TURNER), 2537.

2:6-Diacetoxymercuri-*p*-*iso*amylphenol, and its potassium salt (HENRY and SHARP), 2435.

2:6-Diacetoxymercuri-*p*-*tert.*-butylphenol (HENRY and SHARP), 2434.

Diacetoxymercuricarvacrol (HENRY and SHARP), 2436.

Di-(acetylaminobenzenediazonium chlorides)-antimony *tri*chloride (GRAY), 3177.

Diacetylsuccinic acid, ethyl ester, absorption spectra of (MORTON and ROGERS), 713.

Diamines, diazotised, action of antimony trichloride on (GRAY), 3174.

4:4′-Dianilinodiphenyl, **3:3′-*di*nitro-** (LE FÈVRE and TURNER), 2048.

9:10-Dianilino-9:10-diphenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3083.

9:10-Di-*p*-anisylanthracene (INGOLD and MARSHALL), 3086.

9:10-Di-*p*-anisyl-9:10 dihydroanthracene, 9:10-*di*hydroxy- (INGOLD and MARSHALL), 3086.

Di-*p*-anisyltelluri*di*chloride (MORGAN and KELLETT), 1085.

***p*-Diazoiminobenzene**, salts of (GRAY), 3178.

4-Diazomethylaminodiphenyl (BELL, KENYON, and ROBINSON), 1246.

5-Diazo-3-propyl-1:2:4-triazoles, chloroaurates of (REILLY and DRUMM), 1735.

9:10-Dibenzoyl-9:10-dihydroanthracene (COOK), 1683.

Dibenzoylmethanes, substituted, hydrolysis of (BRADLEY and ROBINSON), 2356.

10:10′-Dibenzoyl-9:9′:10:10′-tetrahydro-9:9′-dianthranyl, and its diacetate (COOK), 1680.

4:4′-Di-1″:2″:3″-benztriazolyldiphenyl (TUCKER), 3036.

Dibenzyl. See *s*-Diphenylethane.

Dibenzylacetic acid, methyl ester (HILL), 956.

Dibenzylacetoacetic acid, ethyl ester, reduction of (HILL), 956.

Dibenzyldimethylammonium picrate (GOSS, INGOLD, and WILSON), 2462.

Dibenzylethylbutylstannane (LAW), 3243.

Dibenzyl ketone δ-anilinosemicarbazone (BAIRD and WILSON), 2373.

Dicarbazyls (TUCKER), 3033.

Dicarbethoxyaminodiphenyl ***p*-*di*-sulphide** (CHILD and SMILES), 2698.

Dicarbomethoxyaminodiphenyl ***p*-*di*-sulphoxide** (CHILD and SMILES), 2698.

Dicarbomethoxyarabinose carbonate (HAWORTH and MAW), 1752.

Dicarboxy*cyclo*pentenylmalonic acid, ethyl ester (INGOLD, SHOPPEE, and THORPE), 1487.

Dicarboxy*cyclo*pentylidenemalonic acid, ethyl ester (INGOLD, SHOPPEE, and THORPE), 1487.

βδ-Dicarboxysuberic acid (INGOLD and SHOPPEE), 1917.

***dl*-Dicentrine**, resolution of (HAWORTH, PERKIN, and RANKIN), 29.

Di-*o*-diphenylenesilicium (WIDDOWSON), 958.

Dielectric constants of mixed organic liquids (KERR), 2796.

2:3-Diethoxybenzyl alcohol, and 5-bromo- and 5-nitro- (RUBENSTEIN), 650.

2:3-Diethoxycinnamic acid, and 5-nitro- (RUBENSTEIN), 652.

Diethyl ketone δ-anilinosemicarbazone (BAIRD and WILSON), 2371.

Difluorescein (DUTT), 1180.

Di*cyclo*hexylphenylarsine, and its derivatives (ROBERTS, TURNER, and BURY), 1446.

Dihomopiperonylamine, ***di*nitro-** (PERKIN, RÂY, and ROBINSON), 948.

Dihydroanthraphenone, derivatives of (COOK), 1681.

9:10-Dihydroanthraphenone, **9:10-*di*chloro-** and **-*di*nitro-** (COOK), 1286.

7:12-Dihydrobenzophenarsazine, 12-chloro- (BURTON and GIBSON), 2243.

Dihydrocodeine, ***di*hydroxy-**, and its triacetyl derivative (CAHN and ROBINSON), 910.

Dihydrodeoxytetrahydro-α-methylmorphimethine, and its salts (CAHN), 2567.

Dihydrodianthranyl, and ***di*bromo-**, ***di*chloro*di*nitro-**, and nitro- (MATTHEWS), 239.

Dihydrodibenzphenarsazines, chloro- (BURTON and GIBSON), 462.

Dihydro-dihydrothebainonemethine, and its *per*chlorate (CAHN), 2571.
4:5-Dihydroiminazole-2-thioglycollic acid, esters and lactam of (STEPHEN and WILSON), 2535.
Dihydromethyldihydrothebainonemethine, and its derivatives (CAHN), 2570.
Dihydropentazines, substituted (CHATTAWAY and PARKES), 113.
5:10-Dihydrophenarsazine, 10-bromo- and 10-iodo- (BURTON and GIBSON), 463.
10-chloro-, and its derivatives (BURTON and GIBSON), 450, 464, 2241.
di- and *tri*-chloro- and 10-chloro-1-amino-, hydrochlorides (BURTON and GIBSON), 2245.
***iso*Dihydroprotopine** chlorides (HAWORTH and PERKIN), 1781.
1:2-Dihydroquinaldine, synthesis of (MASON), 955.
Dihydrosuberocolic acids (GOSS and INGOLD), 1474.
3:5-Diketo-1-benzyl*cyclo*hexane (LINSTEAD and WILLIAMS), 2743.
1:3-Diketodecahydronaphthalene (KON and QUDRAT-I-KHUDA), 3071.
1:3-Diketodecahydronaphthalene-4-carboxylic acid, ethyl ester (KON and QUDRAT-I-KHUDA), 3071.
2:4-Diketo-3:5-diphenyltetrahydrothiazole-2-*iso*propylidenehydrazone (STEPHEN and WILSON), 2534.
β-Diketones, carboxylated (MORGAN and PORTER), 1256.
2:4-Diketo-3-phenyl-5-ethyltetrahydrothiazole, and its 2-*iso*propylidene-hydrazone (STEPHEN and WILSON), 2534.
2:4-Diketo-3-phenyltetrahydrothiazole-2-*iso*propylidenehydrazone (STEPHEN and WILSON), 2534.
2:4-Diketotetrahydrothiazole, 3-amino-, and its hydrazone, hydrochlorides and benzylidene derivatives (STEPHEN and WILSON), 2538.
***leuco*-Dimalachite-green**, and its diacetate (DUTT), 1179.
Di-Meldola's blue (DUTT), 1180.
αα′-Dimethoxyazelaic acid, and its silver salt and derivatives (GOSS and INGOLD), 1476.
2:3-Dimethoxybenzoic acid, 5-amino- (RUBENSTEIN), 652.
3:4′-Dimethoxybenzophenone (LEA and ROBINSON), 2355.
2:3-Dimethoxybenzyl alcohol, 5-bromo- and 5-nitro- (RUBENSTEIN), 649.
2(2:3-Dimethoxybenzylidene)-1-hydrindone (PERKIN, RÂY, and ROBINSON), 952.
2:3-Dimethoxycinnamic acids, 5- and 6-nitro-, and their ethyl esters (RUBENSTEIN), 652.
Dimethoxydiazobenzenesulphonic acids, ammonium salts (PERKIN and RUBENSTEIN), 359.
6:7-Dimethoxy-1-(β-dimethylaminoethyl)phenanthrene, and its salts (ROBINSON and SHINODA), 1994.
5:5′-Dimethoxydiphenyl *di*sulphides, 2:2′- and 4:4′-*di*nitro- (HODGSON and HANDLEY), 543.
3′:4′-Dimethoxyflavylium salts, and 7-hydroxy- (ROBERTSON and ROBINSON), 1952.
1:3-Dimethoxy-5-*cyclo*hexane-0:1:2-*spirobicyclo*pentene, 4-nitro- (HASSELL and INGOLD), 1840.
5:6-Dimethoxy-1-hydrindone, 2-bromo-, and 2-cyano- (PERKIN, RÂY, and ROBINSON), 948.
5:6-Dimethoxy-1-hydrindone-2-carboxylic acid, ethyl ester (PERKIN, RÂY, and ROBINSON), 949.
5:6-Dimethoxy-1-hydrindoneresorcinol (PERKIN, RÂY, and ROBINSON), 949.
Dimethoxy*di*hydroxydistyryl ketones (MCGOOKIN and SINCLAIR), 1579.
3:7-Dimethoxy-2:6-*di*hydroxythianthren *di*sulphide, and its diacetyl derivative (SEN and RÂY), 1140.
2:3[5:6-Dimethoxyindeno(1:2)]dimethoxybenzopyrylium ferrichlorides (PERKIN, RÂY, and ROBINSON), 952.
2:3[5:6-Dimethoxyindeno(1:2)]-8-methoxybenzopyrylium ferrichloride (PERKIN, RÂY, and ROBINSON), 953.
2:3[5:6-Dimethoxyindeno(1 2)]-6:7-methylenedioxybenzopyrylium ferrichloride (PERKIN, RÂY, and ROBINSON), 952.
5:6-Dimethoxyindole-2-carboxylic acid, ethyl ester (PERKIN and RUBENSTEIN), 360.
3:4-Dimethoxy-α-methylcinnamaldehyde, 6-nitro- (WILLIMOTT and SIMPSON), 2810.
6:7-Dimethoxy-1-(3′:4′-methylenedioxy-ω-cyanobenzyl)-2-methyltetrahydro-*iso*quinoline (EDWARDS), 744.
7:4′-Dimethoxy-2-methyl*iso*flavone, 5-hydroxy- (BAKER and ROBINSON), 2718.
6:7-Dimethoxy-3-methylquinoline, and its salts (WILLIMOTT and SIMPSON), 2810.
Dimethoxyphenylhydrazines, and their hydrochlorides (PERKIN and RUBENSTEIN), 357.
β-3:4-Dimethoxyphenyl-α-methylhydracrylaldehyde, β-6-nitro- (WILLIMOTT and SIMPSON), 2810.

Dimethoxyphenylhydrazinosulphonic acids, ammonium salts (PERKIN and RUBENSTEIN), 359.

3:4-Dimethoxyphenyl 3:4-methylenedioxy-β-phenyl-α-aminoethyl ketone, and its salts and derivatives (CAMPBELL, HAWORTH, and PERKIN), 38.

3:4-Dimethoxyphenyl 3:4-methylenedioxy-β-phenylethyl ketone, and its derivatives (CAMPBELL, HAWORTH, and PERKIN), 37.

αα′-Dimethoxypimelic acid, silver salt and ethyl ester of (HASSELL and INGOLD), 1469.

αα′-Dimethoxypimelic acids, and their amides (HASSELL and INGOLD), 1470.

3′:4′-Dimethoxystilbene, 4-chloro-2-amino-, 4-chloro-2:6′-*di*amino-, acetyl derivative, 4-chloro-2-nitro-, 4-chloro-2:6′-*di*nitro-, 2-nitro-4-amino-, and their salts and derivatives (ASHLEY), 2805.

7:4′-Dimethoxy-2-styryl-6-methyl*iso*flavone, 5-hydroxy-, and its acetyl derivative (BAKER and ROBINSON), 2719.

3:4-Dimethoxystyryl veratryl ketone (PERKIN, RÂY, and ROBINSON), 951.

αα′-Dimethoxysuberic acids (GOSS and INGOLD), 1475.

***i*-Dimethoxysuccinic acid,** methyl ester and amide (HAWORTH and HIRST), 1865.

Dimethoxysuccinic acids, bornyl esters, and their rotation (PATTERSON, FULTON, and SEMPLE), 3224.

6:7-Dimethoxytetrahydrocarbazole (PERKIN and RUBENSTEIN), 360.

***p*-Dimethylamino-*p′p″*-*di*aminotriphenylmethane** (DUTT), 1175.

***p*-Dimethylaminobenzaldehyde** methiodide (FAIRBOURNE and WOODLEY), 3241.

4-Dimethylaminobenzaldehyde, 3-bromo- and 3-nitro-, condensation of ethyl acetoacetate with ammonia and (HINKEL and MADEL), 161.

***p*-4-Dimethylaminobenzeneazo-*p′p″*-*di*aminotriphenylmethane** (DUTT), 1175.

***p*-Dimethylaminobenzylidene pentaerythritol,** and its methiodide (FAIRBOURNE and WOODLEY), 3240.

4-Dimethylaminodiphenyl, and its amino-, nitro-, and nitroso-derivatives and their derivatives (BELL and KENYON), 2707.

4-Diethylaminodiphenyl, bromo- (KENYON AND ROBINSON), 3052.

6′-Dimethylaminodiphenylarsinic acid, 2-bromo- (BURTON and GIBSON), 458.

4-*p*-Dimethylaminophenyl-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylic acid, 4-*m*-bromo- and 4-*m*-nitro-, ethyl esters (HINKEL and MADEL), 162.

4-*p*-Dimethylaminophenyl-2:6-dimethylpyridine-3:5-dicarboxylic acid, 4-*m*-bromo-, and 4-*m*-nitro-, ethyl esters (HINKEL and MADEL), 163.

4-Dimethylamino-9-styrylxanthylium chloride, 3:6-*di*hydroxy- (ATKINSON and HEILBRON), 683.

Dimethylaniline, *p*-iodo-, action of nitrous acid on, and 4-iodo-2-nitro- (AITKEN and READE), 1896.

4:4′-Dimethylanilinodiphenyl, 3:3′-*di*nitro- (LE FÈVRE and TURNER), 2048.

***NN*-Dimethyl-*o*-anisidine,** 4-nitro- (C. K. and E. H. INGOLD), 1326.

2:6-Dimethylbenzbisthiazole *hexa*bromide (HUNTER), 535.

3:5-Dimethylbenzthiazole, 1-amino-, and its tetrabromide (HUNTER), 1399.

2:8-Dimethyl-5:10-dihydrophenarsazine, 10-chloro-, and its 5-acetyl derivative (BURTON and GIBSON), 468.

Dimethyl glucose, new crystalline form of (HAWORTH and SEDGWICK), 2573.

γη-Dimethyloctan-ε-one (JONES), 2769.

1:1-Dimethyl-Δ³-*cyclo*penten-2-ol-4-one, and 3-bromo- (ROTHSTEIN and THORPE), 2017.

2:8-Dimethylphenarsazinic acid, and its salts and *N*-acetyl derivative (BURTON and GIBSON), 469.

10:10-Dimethylphenoxarsonium iodide (ROBERTS and TURNER), 1209.

***dl-cis*-2:5-Dimethylpiperazine,** preparation and resolution of, and its derivatives (KIPPING and POPE), 1076.

***trans*-2:5-Dimethylpiperazine,** formation of, from *dl*-alanine (KIPPING and POPE), 494.

***d*- and *l-cis*-2:5-Dimethylpiperazine-*d*-bismethylenecamphor** (KIPPING and POPE), 1078.

2:5-Dimethyl-2-*iso*propenyl*cyclo*hexanone, and its semicarbazone (KON and NUTLAND), 3110.

3:6-Dimethyltetrahydrocarbazole, and its picrate (OAKESHOTT and PLANT), 1213.

Di-β-naphthylvinyl ketone (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2257.

Diphenic acid, β-*di*nitro-, constitution and resolution of, and its derivatives (CHRISTIE, HOLDERNESS, and KENNER), 671.

4:6:4′-*tri*nitro-, and **4:6:4′:6′-*tetra*nitro-,** and their derivatives (CHRISTIE and KENNER), 473.

Diphenoxtellurylium sulphates (DREW), 3067.

***pp′*-Diphenoxydiphenyl *di*telluride** (DREW), 228.

4:4′-Diphenoxydiphenyl, 3:3′-*di*nitro- (LE FÈVRE and TURNER), 2048.

***pp′*-Diphenoxydiphenyltelluri*di*chloride** (DREW), 227.

Diphenyl, space formula of (LE FÈVRE and TURNER), 2476.

Diphenyl, 4-amino-, and 4-hydroxyl-amino-, and their derivatives (BELL, KENYON, and ROBINSON), 1243.

3:4-*di*amino-, and its derivatives, 4-amino-4′-hydroxy- and 3-nitro-4-amino-, derivatives of (BELL and KENYON), 2708.

3:5-*di*bromo-, *mono*-, *di*- and *tri*-bromo-amino-, 3:4-*di*chloro-, *mono*-, *di*-, and *tri*-chloroamino-, and their acetyl derivatives (SCARBOROUGH and WATERS), 557.

bromoamino-, bromonitroamino-, and chloroamino-derivatives (KENYON and ROBINSON), 3050.

bromoamino-, bromonitro-, bromo-nitroamino-, chloronitro- and chloronitroamino-, and their derivatives (LE FÈVRE and TURNER), 2043.

4:4′-*di*bromo-2:3′-*di*amino-, 4:4′-*di*-bromo-2:3′-*di*nitro-, 4:4′-*di*chloro-2:3′-*di*nitro-, and their derivatives (DENNETT and TURNER), 478.

4-chloro-3:3′-*di*nitro-4′-amino-, and 4:4′-*di*chloro*di*nitro-, isomeric, and 3:5′-*di*nitro-4′-amino-4-hydroxy- (HODGSON and GOROWARA), 1754.

4-hydroxy-, derivatives of (BELL and KENYON), 3044.

*di*iodonitro-derivatives (HODGSON), 2385.

Diphenyl series, orientation in (DENNETT and TURNER), 476; (BELL, KENYON, and ROBINSON), 1239; (HODGSON and GOROWARA), 1754; (LE FÈVRE and TURNER), 1759, 2041; (HODGSON), 2384; (BELL and KENYON), 2705, 3044; (KENYON and ROBINSON), 3050.

Diphenylamine, *pp′*-*di*chloro- (BURTON and GIBSON), 2246.

Diphenylamine-*p*-arsinic acid, and its *N*-acetyl derivative (BURTON and GIBSON), 460.

δ-Diphenylaminosemicarbazide hydrochloride, benzylidene derivative (BAIRD and WILSON), 2375.

Diphenylanisylmethoxyphosphorus *di*chlorides (BOYD and SMITH), 2329.

Diphenyl-*p*-anisylmethylphosphinic acid (BOYD and SMITH), 2329.

9:10-Diphenylanthracene, bromo- and chloro-derivatives (INGOLD and MARSHALL), 3085.

Diphenylarsinic acid, 2-bromo-6′-amino- and -6′-nitro- (BURTON and GIBSON), 457.

1:3-Diphenylbarbituric acid, 5-bromo-, hydrazide (MACBETH, NUNAN, and TRAILL), 1252.

Diphenylbenzidine, *di-o*-amino- and *di-o*-nitro-, and their derivatives (TUCKER), 3034.

***d*-αβ-Diphenyl-αβ-dibenzylethyl alcohol** (MCKENZIE, ROGER, and WILLS), 790.

Diphenyl-3:3′-dicarboxylic acid, 2:2′-*di*nitro-, and its ethyl ester (BURTON, HAMMOND, and KENNER), 1804.

9:10-Diphenyl-9:10-dihydroanthracene, and its metallic derivatives and bromohydroxy-, *di*chloro*di*bromo-, and chlorohydroxy-derivatives (INGOLD and MARSHALL), 3085.

1:5-Diphenyl-1:4-dihydropentazine, 1-2:4-*di*bromo- (CHATTAWAY and PARKES), 116.

***s*-Diphenylethane**, 3:4′-*di*amino-, and its derivatives (HARRISON), 1236.

αβ-Diphenylethyl alcohol, 3:4′-*di*nitro- (HARRISON and WOOD), 580.

3:5-Diphenylimino-2:4-diphenyltetrahydro-1:2:4-thiodiazole *octa*bromide and *hexa*iodide (HUNTER), 536.

Diphenylnaphthylmethoxyphosphorus *di*chlorides (BOYD and SMITH), 2330.

Diphenylnaphthylmethylphosphinic acids, and their salts (BOYD and SMITH), 2331.

***r*- and *l*-αα-Diphenyl-*n*-propyl alcohols, β-amino-** (MCKENZIE, ROGER, and WILLS), 786, 790.

Diphenyl *di*sulphide *pp′*-diarsinic acid, and its barium salt (HEWITT, KING, and MURCH), 1369.

1:4-Diphenyl-1:2:3:5-tetrazole, 1-2:4-*di*bromo- and 1-2:4-*di*bromo-4-*m*-nitro- (CHATTAWAY and PARKES), 114.

***s*-Diphenylthiocarbamide**, *di*-2:3-*di*chloro- and -3:4:5-*tri*chloro- (DYSON, GEORGE, and HUNTER), 3042.

5:7-Diphenylthiol-8-hydroxyquinoline, bis-2′:5′-*di*chloro- (BROOKER and SMILES), 1729.

2:4-Diphenylthiol-1-naphthol, chloro-derivatives (BROOKER and SMILES), 1728.

Diphenyl-*p*-tolylmethoxyphosphorus *di*chloride (BOYD, SMITH, and TULLY), 2331.

Diphenyl-*p*-tolylmethylphosphinic acid, and its potassium salt (BOYD and SMITH), 2332.

Diphenylyl-4-acetylchloroamine (BELL, KENYON, and ROBINSON), 1246.

Diphenylylphenylthiocarbamide, 4′-amino- (LE FÈVRE and TURNER), 2484.
Diphenylylthiocarbamic acid 4′-amino-, phenyl ester (LE FÈVRE and TURNER), 2483.
Diphthalylbenzidine, nitration of (HODGSON), 2384.
Dipiperonyl*iso*butyrophenone, *di*-ω-6-nitro- (PERKIN, RÂY, and ROBINSON), 947.
3:3′-Di-*n*-propyl-5:5′-azo-1:2:4-triazole (REILLY and DRUMM), 1733.
Di*iso*propylidenemannose, rotation and methylation of (IRVINE and SKINNER), 1089.
Di-*n*- and -*iso*-propyl ketones, δ-anilino-, semicarbazones of (BAIRD and WILSON), 2372.
Dipyronine G (DUTT), 1179.
Disaccharides, constitution of (COOPER, HAWORTH, and PEAT), 876; (HAWORTH and PEAT), 3094.
Dispersoids, fixation of methylene-blue by (FODOR and RIWLIN), 102.
Ditellurodipropionic acid, and its salts (MORGAN and KELLETT), 1088.
4:4′-Ditolyl, nitro-derivatives (DENNETT and TURNER), 480.
9:10-Di-*p*-tolylanthracene, and its potassium and sodium derivatives (INGOLD and MARSHALL), 3085.
9:10-Di-*p*-tolyl-9:10-dihydroanthracene, 9:10-*di*hydroxy- (INGOLD and MARSHALL), 3085.
5:7-Di-*p*-tolylthiol-8-hydroxyquinoline (BROOKER and SMILES), 1729.
Di-*p*-tolylthiolphenylacetonitrile (BROOKER and SMILES), 1726.
Dodecahydrosqualene (HEILBRON, HILDITCH, and KAMM), 3135.
Drying, intensive, effect of, on inner equilibria (SMITS), 2655; (SMITS, DE LIEFDE, SWART, and CLAASSEN), 2657.

E.

Earths, rare, ultra-violet spectra of (GARDINER), 1518.
Elaidic acid, oxidation of, and its derivatives (HILDITCH), 1828.
Electrochemical phenomena, periodic, at copper and silver anodes (HEDGES), 1533.
Electrodes, hydrogen, precipitation studies with (BRITTON), 125.
Electrolysis, alternating current, arrangement for (SAND and LLOYD), 2971.
Electrolytes, strong, hydration of, and viscosity of their aqueous solutions (SUGDEN), 174.
Electrolytic polarisation (GLASSTONE), 2857, 2897.
Emulsions, photographic. See under Photographic.
Equilibria, inner, effect of intensive drying on (SMITS), 2655; (SMITS, DE LIEFDE, SWART, and CLAASSEN), 2657.
Erbium, ultra-violet spectrum of (GARDINER), 1518.
Esters, alkaline hydrolysis of, in aqueous alcoholic solution (GYNGELL), 2484.
Esters, sparingly soluble, rate of hydrolysis of (SMITH and PATERSON), 940.
Ethane, *s-tetra*bromo-, action of, on organic bases (FULTON), 197.
Ethanolbisethylenediaminocupric iodide, and its thermal properties (MORGAN, CARTER, and HARRISON), 2028.
2-Ethoxyanisole, 4:5-*di*nitro- (ALLAN and ROBINSON), 378.
4-Ethoxyanisole, nitro-derivatives (ROBINSON and SMITH), 395.
2-Ethoxybenzaldehyde, 5-nitro-, semicarbazone (CHATTAWAY), 2725.
crystallography of (CHATTAWAY and CURJEL), 3214.
2-Ethoxybenzoic acid, 5-nitro- (CHATTAWAY), 2724.
10-Ethoxy-1-hydroxy-4:9-anthraquinone (GREEN), 1434.
α-Ethoxymethylsuccinamide (INGOLD, SHOPPEE, and THORPE), 1487.
***dl*-2-Ethoxyphenylglycollic acid**, 5-nitro-, and its silver salt and acetyl derivative (CHATTAWAY), 2724.
2-*p*-Ethoxyphenylpyridine, and its picrate (FORSYTH and PYMAN), 2918.
Ethyl alcohol, equilibria of, with alkali and alkaline-earth salts (BONNELL and JONES), 318.
influence of dissolved salts on miscibility temperatures of mixtures of paraffins with (HOWARD and PATTERSON), 2787.
action of iodine on, in presence of aluminium and water (JONES and GREEN), 2760.
reactions of, with substituted carbamyl chlorides (PRICE), 3230.
Ethyl ether, flame spectra of (EMELÉUS), 2948.
iodide, preparation of (JONES and GREEN), 2760.
reactions of, with sodium phenoxides in alcoholic solution (GOLDSWORTHY), 1254.
hydrogen sulphate (HAMID, SINGH, and DUNNICLIFF), 1098.
1-Ethylaminobenzthiazole, and its *di*-bromide (HUNTER), 2954.

1-Ethylaminobenzthiazole, 5-bromo-, and its *di*bromide (HUNTER and SOYKA), 2962.
2-Ethylamino-β-naphthathiazole, and its *tetra*bromide (DYSON, HUNTER, and SOYKA), 2966.
9-Ethylcarbazole, 3:6-*di*iodo- (TUCKER), 552.
***p*-Ethylcarbonato-*m*-methoxybenzoic acid**, and its anhydride (HEAP and ROBINSON), 2343.
2-Ethyl-1:2-dihydrobenzthiazole, 1-imino-, and its bromides (HUNTER), 1394.
Ethylene, reaction of bromine with (NORRISH and JONES), 55.
bromohydrin, preparation of (MCDOWALL), 499.
Ethylene*di*aminobisacetylacetone, compounds of, with copper, nickel, and palladium salts (MORGAN and SMITH), 918.
Ethylenebisacetylacetone, keto-enolic isomerism of, and its oximes (MORGAN and TAYLOR), 43.
Ethylenediamine, complex copper salts with (MORGAN and BURSTALL), 2018.
compounds of, with copper, nickel, and palladium compounds of ethylenediaminobisacetylacetone (MORGAN and SMITH), 918.
Ethyl-α-Δ¹-*cyclo*hexenylmethyl ethyl ketone semicarbazone (KON and SMITH), 1797.
1-Ethylimino-1:2-dihydrobenzthiazole *di*bromide (HUNTER and SOYKA), 2962.
2-Ethyl-2-Δ¹-*cyclo*pentenyl*cyclo*pentanone, and its derivatives (KON and NUTLAND), 3107.
2-Ethyl-2-*iso*propenyl*cyclo*pentanone, and its semicarbazone (KON and NUTLAND), 3108.
α-Ethylstyrene (JOHNSON and KON), 2755.
***o*-Ethylsulphonylbenzenesulphonamide** (HURTLEY and SMILES), 1824.
Europium, ultra-violet spectrum of (GARDINER), 1518.
Explosion of gaseous mixtures (CAMPBELL and WOODHEAD), 3010.

F.

Filtration of small amounts of material (HARTUNG), 840.
Fisetin, synthesis of, and its derivatives (ALLAN and ROBINSON), 2334.
Fish, elasmobranch, constituents of oils from (HEILBRON, KAMM, and OWENS), 1630; (HEILBRON, HILDITCH, and KAMM), 3131; (HARVEY, HEILBRON, and KAMM), 3136.
Fish liver oils (HEILBRON, KAMM, and OWENS), 1630.
Flame, propagation of, in mixtures of methane and air (CHAPMAN and WHEELER), 2139.
Flavone, 3:7:3′:4′-*tetra*hydroxy-, tetra-acetyl derivative (ALLAN and ROBINSON), 2335.
***iso*Flavone group**, syntheses in (BAKER and ROBINSON), 2713.
Flavylium salts, hydroxy- (ROBERTSON and ROBINSON), 1951.
Fluorene, absorption spectrum of (CAPPER and MARSH), 724.
Fluorene, 2:5- and 2:7-*di*amino-, and their acetyl derivatives, and 2:5- and 2:7-*di*nitro- (MORGAN and THOMASON), 2691.
Fluorine:—
Hydrofluoric acid, action of, on selenium and tellurium compounds (PRIDEAUX and MILLOTT), 167, 520.
Hydrofluozirconic acid (PRIDEAUX and ROPER), 898.
Formic acid, photochemical decomposition of aqueous solutions of (ALLMAND and REEVE), 2852.
velocity of reaction of iodine with (HAMMICK and ZVEGINTZOV), 1105.
sodium salt, reduction of silver acetate by (COUTIE), 887.
methyl ester, equilibrium between methyl alcohol and (CHRISTIANSEN), 413.
Formic acid, *trithio*-, ethylene ester (HURTLEY and SMILES), 2268.
2-Formyl-6-methylquinoline, *p*-nitrophenylhydrazone of (HUMPHRIES), 376.
Formylphenylacetic acid, ethyl ester, absorption spectra of (MORTON and ROGERS), 713.
Fructose. See Lævulose.
γ-Fructose, structure of (HAWORTH and HIRST), 1858.
α-Furoylpiperonylcarbinyl benzoate (GREENE), 335.

G.

Galangin, synthesis of (HEAP and ROBINSON), 2337.
Gases, absorption of, by colloidal solutions (GATTERER), 299.
ignition of, by explosion (CAMPBELL and WOODHEAD), 3010.
Gas circulation apparatus (GREEN), 500.
Gas reactions, termolecular (HINSHELWOOD and GREEN), 730.

Genistein, constitution of, and its identity with prunetol (BAKER and ROBINSON), 2713.

Germanium *tetra*chloride, and its ammonia compounds (PUGH and THOMAS), 1051.

Germanic acid, salts (PUGH), 2828.

Glass, physical properties, composition and preparation of various kinds of (TURNER), 2091.

β-Gluconolactone, structure of (HAWORTH and NICHOLSON), 1899.

Glucose. See Dextrose.

4′-β-Glucosidoxy-7-hydroxy-3-methoxyflavylium chloride, and its 4′-tetra-acetyl derivative (ROBERTSON and ROBINSON), 1717.

4′-β-Glucosidoxy-7-hydroxy-3-methoxy-5-methylflavylium chloride, and its 4′-tetra-acetyl derivative (ROBERTSON and ROBINSON), 1719.

β-Glucosidoxy-ω-methoxyacetophenone, *p*-tetra-acetyl derivative (ROBERTSON and ROBINSON), 1715.

Glutaconic acids, chemistry of (PACKER and THORPE), 1199; (FARMER and RICHARDSON), 2172.

α-Glycerides, oxidation of allyl esters to (FAIRBOURNE and FOSTER), 3146.

β-Glycerides, α-structure of (FAIRBOURNE and FOSTER), 3148.

Glycerol *di*bromohydrin, chlorohydrin, and *di*chlorohydrin nitrobenzoates (FAIRBOURNE and FOSTER), 3150.

Glycine, butyl esters, and their derivatives (MORGAN), 80.

Glycols, dehydration of (MCKENZIE and DENNLER), 1596.

Gold, interaction of hydrogen and nitrous oxide on the surface of (HUTCHISON and HINSHELWOOD), 1556.

Aurous oxide, existence of (POLLARD), 1347.

Chloroauric acid, action of mercurous nitrate on (POLLARD), 529.

Guaiacol, 3- and 6-amino- and -nitro-derivatives, and their derivatives (OXFORD), 2004.

5-nitrothio- (HOLMES, C. K. and E. H. INGOLD), 1689.

Guanidine, hydrolysis of (BELL), 1213.

H.

Hæmatoxylin, synthesis of, and its derivatives (PERKIN, RÂY, and ROBINSON), 941.

Hæmoglobin (BARCROFT), 1146.

Halides, estimation of, electrometrically (CLARK), 749.

Halogens, lability of, in organic compounds (MACBETH, NUNAN, and TRAILL), 1248.

Halogen organic compounds, action of alkaline arsenites on (BALABAN), 569.

Halogenation of phenols (SOPER and SMITH), 1582.

Heat of crystallisation of fatty acids (GARNER, MADDEN, and RUSHBROOKE), 2491.

n-**Heptaldehyde** δ-anilinosemicarbazone and methylphenylhydrazone (BAIRD and WILSON), 2870.

1-*n*-**Heptylaminobenzthiazole**, and its dibromide hydrobromide (HUNTER), 2957.

1-*n*-**Heptylaminobenzthiazole**, 5-bromo-, and its oibromide (HUNTER and SOYKA). 2964.

2-*n*-**Heptylamino-β-naphthathiazole**, and its tetradecabromide (DYSON, HUNTER, and SOYKA), 2969.

Hexabenzyldistannane (LAW), 3243.

Hexahydrobenzylideneacetone semicarbazide-semicarbazone and semicarbazone (KON and SMITH), 1799.

n-**Hexane**, effect of intensive drying on (SMITS, DE LIEFDE, SWART, and CLAASSEN), 2666.

*cyclo***Hexane-1-acetic-1-propionic acid**, and its calcium salt, and ethyl ester (NORRIS), 250.

*cyclo***Hexane-1-acetone-1-acetic acid**, and its semicarbazone (NORRIS), 248.

*cyclo***Hexane***spiro*-3-**bromo-Δ²-*cyclo*penten-2-ol-4-one** (ROTHSTEIN and THORPE), 2017.

*cyclo***Hexane***spiro*-3:5-*di*chloro-Δ²·⁴-*cyclo*-**hexadiene** (NORRIS), 253.

*cyclo***Hexane***spiro*-5-**chloro-Δ⁴-*cyclo*-hexen-3-one**, and its semicarbazone (NORRIS), 248.

*cyclo***Hexane-1:1-dicarboxylic acid**, esters (WIGHTMAN), 2543.

*cyclo***Hexane***spirocyclo***hexan-3:5-dione**, reactions of (NORRIS), 248.

*cyclo***Hexane***spirocyclo***hexane** (NORRIS), 245.

*cyclo***Hexane***spirocyclo***hexan-3-ol**, and its *p*-nitrobenzoate (NORRIS), 249.

*cyclo***Hexane***spirocyclo***hexan-3-one**, and its derivatives (NORRIS), 249.

*cyclo***Hexane***spirocyclo***pentane-2:4-dione** (ROTHSTEIN and THORPE), 2016.

5-*cyclo***Hexane***spiro*-0:1:2-*bicyclo***pentene-1:3-diol**, 4-nitro- and 4-nitroso- (HASSELL and INGOLD), 1839.

5-*cyclo***Hexane***spirocyclo***penten-3-ol**, 1:4-*di*oximino- (HASSELL and INGOLD), 1839.

5-*cyclo*Hexane*spirocyclo*penten-3-ol-1-one, 4-oximino- (HASSELL and INGOLD), 1839.

***cyclo*Hexanone δ-anilinosemicarbazone** (BAIRD and WILSON), 2371.

carboxyphenylhydrazones (COLLAR and PLANT), 808.

α-Δ¹-*cyclo*Hexenylacetophenone, and its derivatives (FARROW and KON), 2132.

2-Δ¹-*cyclo*Hexenyl*cyclo*hexanone, and its derivatives (KON and NUTLAND), 3104.

Δ¹-*cyclo*Hexenylmalonic acid, ethyl ester (KON and SPEIGHT), 2733.

α-Δ¹-*cyclo*Hexenylmethyl ethyl ketone semicarbazone (KON and SMITH), 1797.

1-*n*-Hexylaminobenzthiazole, and its dibromide (HUNTER), 2957; (HUNTER and SOYKA), 2964.

2-*n*-Hexylamino-β-naphthathiazole, and its tetrabromide hydrobromide (DYSON, HUNTER, and SOYKA), 2969.

α-*cyclo*Hexylbutan-γ-one, α-hydroxy-, and its semicarbazone (KON and SMITH), 1798.

1-*cyclo*Hexyl-3:5-diketo*cyclo*hexane (KON and SMITH), 1799.

1-*cyclo*Hexyl-3:5-diketo*cyclo*hexane-6-carboxylic acid, ethyl ester (KON and SMITH), 1799.

α-*cyclo*Hexylidenebutan-γ-one semicarbazone (KON and SMITH), 1800.

α-*cyclo*Hexylidenebutyronitrile (FARROW and KON), 2134.

***cyclo*Hexylphenylbenzylmethylarsonium salts** (ROBERTS, TURNER, and BURY), 1447.

***Holarrhena*, conessine from species of** (KANGA, AYYAR, and SIMONSEN), 2123.

Homocatechol, derivatives of (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1971; (GULLAND and ROBINSON), 1976.

β-Homochelidonine (α-allo*cryptopine*), formation of, from berberine (HAWORTH and PERKIN), 445.

Homopiperonylresacetophenone, 6′-bromo- (BAKER), 1076.

Homoveratrole, 6-bromo-2-nitro-, and 2-nitro-6-amino-, and its salts and derivatives (GULLAND and ROBINSON), 1979.

2:6-*di*nitro- (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1975.

Homoveratrole-6-sulphonyl chloride, 5-nitro- (GULLAND and ROBINSON), 1977.

3-Homoveratryl-7-methoxychroman (PERKIN, RÂY, and ROBINSON), 946.

Hydration of strong electrolytes (SUGDEN), 174.

Hydrazines, action of, on semicarbazones (BAIRD and WILSON), 2367.

Hydrazinedicarboxymethylamide (COOPER and INGOLD), 1895.

ω-Hydrazinobenzaldehyde-2:4-*di*bromophenylhydrazone, and its derivatives (CHATTAWAY and PARKES), 115.

Hydrazinohomoveratrole, nitro-, and its piperonylidene derivative (GULLAND and ROBINSON), 1980.

***p*-Hydrazinophenylpyridines** (FORSYTH and PYMAN), 2917.

Hydrazobenzaldehyde-2:4-*di*bromophenylhydrazone (CHATTAWAY and PARKES), 116.

Hydrocarbon, $C_{13}H_{14}$, from dehydrogenation of tetra*cyclo*squalene (HARVEY, HEILBRON, and KAMM), 3138.

$C_{18}H_{28}$, from reduction of *iso*phorone (BAKER), 669.

Hydrocarbons, incipient ionisation of hydrogen atoms in (HOLMES and INGOLD), 1305.

aliphatic higher, boiling points of (FRANCIS and WOOD), 1420.

condensed nuclear, absorption spectra of (CAPPER and MARSH), 724.

Hydrocyanic acid. See under Cyanogen.

Hydroferricyanic acid, salts, preparation and estimation of (CUMMING and GOOD), 1924.

Hydroferrocyanic acid, salts, preparation and estimation of (CUMMING and GOOD), 1924.

calcium, potassium, and sodium salts, solubilities of (FARROW), 49.

Hydrofluoric acid. See under Fluorine.

Hydrofluozirconic acid. See under Fluorine.

Hydrogen, ignition of mixtures of carbon monoxide and (CAMPBELL and WOODHEAD), 3010.

interaction of nitric oxide and (HINSHELWOOD and GREEN), 730.

interaction of nitrous oxide and, on the surface of gold (HUTCHISON and HINSHELWOOD), 1556.

Hydrogen fluoride. See Hydrofluoric acid under Fluorine.

*per*oxide, action of, on solutions of potassium permanganate (DUNNICLIFF and NIJHAWAN), 1.

sulphide, improved generator for (DENHAM and PACKER), 1344.

interaction of sulphur dioxide and (MATTHEWS), 2270.

Hydronaphthalenes, stereochemistry of (KAY and STUART), 3038.

Hydroxy-acid, $C_{22}H_{25}O_9N$, and its salts, from narcotine oxide and hydrochloric acid (DRUMMOND and MCMILLAN), 2704.
Hydroxy-compounds, decomposition of substituted carbamyl chlorides by (PRICE), 653, 3230.
Hydroxyl ions, mobility of (RAIKES, YORKE, and EWART), 630.
Hydroxylamine, reaction of ferric chloride with (MITCHELL), 336.
Hystazarin, diacetyl derivative (GREEN), 2202.

I.

Imino-aryl ethers (CHAPMAN), 2296.
2:3-Indeno(1:2)dimethoxybenzopyrylium ferrichlorides (PERKIN, RÂY, and ROBINSON), 951.
Indolinone compounds, relative stability of quinolone compounds and (AESCHLIMANN), 2902.
Iodine, catalysis of the reaction between acetone and (DAWSON and CARTER), 2282; (DAWSON and DEAN), 2872.
action of, on ethyl alcohol in presence of aluminium and water (JONES and GREEN), 2760.
velocity of reaction of formic acid with (HAMMICK and ZVEGINTZOV), 1105.
Ionisation constants, determination of (DAWSON and HOSKINS), 3166.
Iron, electro-deposition potential of (GLASSTONE), 2887.
periodic passivity of (HEDGES), 2878.
removal of, from amalgams (RUSSELL, EVANS, and ROWELL), 1872.
Iron alloys with cobalt and nickel, electro-deposition potentials of (GLASSTONE), 2897.
Iron phosphates (CARTER and HARTSHORNE), 363.
Ferric chloride, reaction of hydroxylamine with (MITCHELL), 336.
Iron organic compounds, complex, with oximes (TAYLOR and EWBANK), 2818.
Isomerism, dynamic (JONES and LOWRY), 720; (FAULKNER and LOWRY), 1938.
Itaconic acid, ethyl ester, action of ethyl sodiomalonate on (INGOLD and SHOPPEE), 1912.

K.

Kaempferide, synthesis of, and its salts and triacetyl derivative (HEAP and ROBINSON), 2336.
α-Ketoazelaic acid (GOSS and INGOLD), 1477.
10-Ketobehenic acid, and its amide (G. M. and R. ROBINSON), 2207.
3-Keto-1:4-benzdithian-2:2′-*spiro*-1′:3′-benzdithiole (HURTLEY and SMILES), 2269.
γ-Ketobutenylnaphthalenes (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2257.
γ-Ketobutylnaphthalenes, and their derivatives (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2258.
2-Keto-1:2-dihydrobenz*iso*thiazole, and its derivatives (MCCLELLAND and GAIT), 921.
α-Ketoglutaric acid, *p*-methoxyphenylhydrazone of (PERKIN and RUBENSTEIN), 362.
2-Keto-1-methyl-1:2-dihydrobenz*iso*-thiazole (MCCLELLAND and GAIT), 923.
4-Ketomyristic acid, and its oxime (G. M. and R. ROBINSON), 2206.
Ketone, $C_{15}H_{20}O_2$, from oxidation of β-caryophyllene (GIBSON, ROBERTSON, and SWORD), 164.
$C_{15}H_{24}O$, and its semicarbazone, from oxidation of β-caryophyllene (GIBSON, ROBERTSON, and SWORD), 164.
$C_{26}H_{52}O$, from oxidation of paraffin wax (FRANCIS and GAUNTLETT), 2381.
$C_{28}H_{56}O$, from oxidation of paraffin wax (FRANCIS and GAUNTLETT), 2381.
$C_{29}H_{58}O$, from oxidation of paraffin wax (FRANCIS and GAUNTLETT), 2381.
Ketones, cyclic, mobility of (KON and NUTLAND), 3101.
optically active, preparation of (MCKENZIE, ROGER, and WILLS), 779.
unsaturated, alkylation of (KON), 1792.
2-Keto-1-methyl-1:2:3:4-tetrahydroquinoline-4-carboxylic acid, and its methyl ester (AESCHLIMANN), 2908.
10-Ketononadecoic acid, and its amide (G. M. and R. ROBINSON), 2207.
4-Keto-3-phenyl-1:2-benzoxazine, 7-nitro- (BISHOP and BRADY), 812.
2-Keto-1-phenyl-1:2-dihydrobenz*iso*-thiazole (MCCLELLAND and GAIT), 923.
3-Keto-2-phenyl-ψ-indole, 6-nitro-, 1-oxide (BISHOP and BRADY), 812.
9-Ketostearic acid (G. M. and R. ROBINSON), 2206.
2-Keto-1:2:3:4-tetrahydroquinoline-4-carboxylic acid, preparation of, and bromo- and iodo-, and their esters (AESCHLIMANN), 2907.
2-Keto-1-*o*-tolyl-1:2-dihydrobenz*iso*-thiazole (MCCLELLAND and GAIT), 923.

Kolbe's synthesis, mechanism of (FAIRWEATHER and WALKER), 3111.

L.

Lactic acid, butyl esters, rotatory dispersion of (WOOD, SUCH, and SCARF), 1928.
Lævulic acids, substituted, *spiro*-compounds from (ROTHSTEIN and THORPE), 2011.
Lævulose, structure of (HAWORTH and HIRST), 1858.
Lead halides, equilibria of potassium halides, water, and (BURRAGE), 1703.
iodide, solubility of, in sodium chloride solutions (BURRAGE), 1896.
germanate (PUGH), 2832.
*sub*oxide (AUFENAST and TERREY), 1546.
Lead anodes. See under Anodes.
Lectures, delivered before the Chemical Society (BARCROFT), 1146; (TURNER), 2091; (SØRENSEN), 2995.
Leucine, butyl esters, and their salts (MORGAN), 83.
Liquids, potentials at junctions of (CARTER and LEA), 834.
vapour pressure of, by a differential method (JOLLY and BRISCOE), 2154.
organic, and their mixtures, dielectric constants of (SAYCE and BRISCOE), 2623.
organic mixed, dielectric constants of (KERR), 2796.
Lithium germanate (PUGH), 2831.
Lutidine, compound of acetylene tetrabromide and (FULTON), 198.

M.

Magnesium anodes. See under Anodes.
Malonic acid, beryllium salt, conductivity of (SIDGWICK and LEWIS), 2539.
ethyl ester, sodium salt, action of, on ethyl citraconate or itaconate (INGOLD and SHOPPER), 1912.
Malonic acids, cyclic and open-chain esters, hydrolysis of (GANT and INGOLD), 10.
Maltose, constitution of (IRVINE and BLACK), 862; (COOPER, HAWORTH, and PEAT), 876; (HAWORTH and PEAT), 3094.
Manganese, removal of, from amalgams (RUSSELL, EVANS, and ROWELL), 1872.
Manganese oxides, hydrates, effect of neutral salts on the electrical charge of, and concentration of hydrogen ions liberated (GHOSH), 2605.
sulphate, equilibrium of potassium sulphate, water, and (CAVEN and JOHNSTON), 2628.
β-Mannonolactone, structure of (HAWORTH and NICHOLSON), 1899.
Mannose diacetone. See Di*iso*propylidenemannose.
***m*-Meconineacetic acid**, and its derivatives (EDWARDS), 748.
Melting point curves of isomerides in the camphor series (ROSS and SOMERVILLE), 2770.
Membranes, nickel, for ultrafiltration (MANNING), 1127.
Menthones, optically active, and their derivatives (READ and ROBERTSON), 2209.
Menthone series (READ and ROBERTSON), 2209; (READ, COOK, and SHANNON), 2223.
Menthylamines, optically active, and their derivatives (READ and ROBERTSON), 2209.
***dl*-Menthylamines**, and their derivatives (READ, COOK, and SHANNON), 2223.
***d*-*iso*Menthylcarbamide** (READ and ROBERTSON), 2222.
***d*-*iso*Menthylphenylcarbamide** (READ and ROBERTSON), 2222.
***dl*-*iso*Menthylphenylcarbamide** (READ, COOK, and SHANNON), 2231.
***d*-*iso*Menthylphenylthiocarbamide** (READ and ROBERTSON), 2222.
Mercaptides, co-ordinated (DRUMMOND and GIBSON), 3073.
Mercuration of alkylphenols and their aldehydes (HENRY and SHARP), 2432.
of aromatic compounds (COFFEY), 637, 3215.
Mercury, critical temperature of (SAYCE and BRISCOE), 957.
Mercury alloys, order of removal of metals from (RUSSELL, EVANS, and ROWELL), 1872.
Mercurous nitrate, action of chloroauric acid with (POLLARD), 529.
Mercury organic compounds:—
4-Mercuribis-2-nitrotoluene (COFFEY), 639.
Mercuri-2-methyl-6-*iso*propylbenzaldehyde, 4-hydroxy-5-chloro- (HENRY and SHARP), 2438.
Mercuri-2-nitrotoluene, 4-bromo-, chloro-, and 4-iodo- (COFFEY), 638.
Mercurinitrotoluenes, chloro- (COFFEY), 3218.

Mercury anodes. See under Anodes.
Mesityl oxide, absorption spectra of (MORTON), 719.
Mesityloxidoxalic acid, ethyl ester, absorption spectra of (MORTON and ROGERS), 713.
Metals, liquid-line corrosion of (HEDGES), 831.
Metallic oxides, finely divided, catalytic decomposition of sodium hypochlorite solutions by (CHIRNOAGA), 1693.
Methane, propagation of flame in mixtures of air and (CHAPMAN and WHEELER), 2139.
extinction of flames of, by diluent gases (COWARD and HARTWELL), 1522.
Methane, halogen derivatives, absorption spectra of (LOWRY and SASS), 622.
Methanolbisethylenediamminocupric iodide (MORGAN and BURSTALL), 2023.
Methoxyacetic acid, β-octyl ester (RULE and MITCHELL), 3207.
3-Methoxyacetophenone, ω:4-*di*hydroxy-, acetyl derivatives (NOLAN, PRATT, and ROBINSON), 1970.
ω-Methoxyacetophenone, *p*-hydroxy- (ROBERTSON and ROBINSON), 1715.
7-Methoxy-4-*p*-anisyl-2-*p*-dimethylaminostyryl-3-methylbenzopyrylium salts (HEILBRON and ZAKI), 1906.
7-Methoxy-4-*p*-anisyl-2:3-dimethylbenzopyrylium salts (HEILBRON and ZAKI), 1905.
7-Methoxy-4-*p*-anisyl-2-*p*-hydroxystyryl-3-methylbenzopyrylium salts (HEILBRON and ZAKI), 1906.
3-Methoxybenzaldehyde, chloro-derivatives, and their derivatives (HODGSON and BEARD), 154.
2-Methoxybenzoic acid, 6-nitro-3-hydroxy- (RUBENSTEIN), 652.
3-Methoxybenzoic acid, 2- and 4-chloro- (GIBSON), 1428.
2:6-*di*chloro- and 6-nitro-, and their derivatives (HODGSON and BEARD), 153.
2-nitro-4-amino-, acetyl derivative (ROBINSON and SHINODA), 1992.
Methoxybenzoic acids, *sec.*-β-octyl esters of, and their rotation (RULE and NUMBERS), 2116.
***p*-Methoxybenzomethylamide,** and its acetyl derivative (BRADY and DUNN), 2416.
ω-Methoxybenzoylacetophenones, and their copper derivatives (BRADLEY and ROBINSON), 2359.
Methoxybenzoylbenzoins (GREENE), 328.
ω-3-Methoxybenzoyl-3:4-dimethoxyacetophenone, and its copper derivative (BRADLEY and ROBINSON), 2366.
ω-3-Methoxybenzoyl-4-methoxyacetophenone, and its copper derivative (BRADLEY and ROBINSON), 2365.
2-*m*-Methoxybenzylidene-5:6-dimethoxy-1-hydrindone (PERKIN, RÂY, and ROBINSON), 950.
2-Methoxybenzyloxyanisoles, nitro-derivatives (OXFORD and ROBINSON), 389.
7-Methoxy-3-(6′-bromohomopiperonyl)-2-methyl-1:4-benzopyrone (BAKER), 1076.
2:3-[7-Methoxychromeno(4:3)]7-6:7-dimethoxybenzopyrylium ferrichloride (PERKIN, RÂY, and ROBINSON), 950.
7-Methoxy-4-*p*-dimethylaminophenyl-2:3-dimethylbenzopyrylium salts (HEILBRON and ZAKI), 1906.
4-Methoxydiphenyl, nitro-derivatives (BELL and KENYON), 3048.
Methoxydiphenyl ethers, and their nitro-derivatives (LEA and ROBINSON), 412.
3-Methoxy-2-ethoxybenzyl alcohol, 5-bromo- and 5-nitro- (RUBENSTEIN), 650.
3-Methoxy-2-ethoxycinnamic acid, and 5-nitro (RUBENSTEIN), 652.
3-Methoxy-2-ethoxyphenanthraphenazine (ALLAN and ROBINSON), 379.
Methoxyethoxyphenyl-4:5-thiotriazopyrocatechol methyl ethyl ether, 6′-nitro- (ALLAN and ROBINSON), 379.
4′-Methoxyflavone, 7-hydroxy-, and its acetyl derivative (ROBINSON and VENKATARAMAN), 2346.
3:7-*di*hydroxy-, and its diacetyl derivative (HEAP and ROBINSON), 2339.
Methoxyflavylium chlorides, *tetra-* and *penta*-hydroxy- (GATEWOOD and ROBINSON), 1964.
3-Methoxyflavylium salts, **7:4′-*di*hydroxy-** (ROBERTSON and ROBINSON), 1716.
3-Methoxy-5-*cyclo*hexane*spirocyclo*pentene-1:4-dione (HASSELL and INGOLD), 1840.
Methoxyhydroxystyryl methyl ketones, and their acetyl derivatives (McGOOKIN and SINCLAIR), 1579.
3-Methoxy-α-methylcinnamaldehyde, 6-nitro- (WILLIMOTT and SIMPSON), 2810.
3-Methoxy-5-methylflavylium salts, **7:4′-*di*hydroxy-** (ROBERTSON and ROBINSON), 1718.
6-Methoxy-3-methylquinoline, and its salts (WILLIMOTT and SIMPSON), 2810.

5-Methoxy-α-naphthaldehyde, and its derivatives (SHOESMITH and RUBLI), 3241.
5-Methoxy-α-naphthoyl chloride (SHOESMITH and RUBLI), 3242.
3-Methoxy-4-oximino-5-*cyclo*hexane-*spirocyclo*pentene-1:4-dione (HASSELL and INGOLD), 1840.
***m*-Methoxyphenol** ethylene ether (PERKIN, RÂY, and ROBINSON), 946.
4-Methoxyphenol, 2- and 3-nitro-, preparation of, and their derivatives (ROBINSON and SMITH), 392.
7-Methoxy-4-phenyl-2-*p*-dimethylaminostyryl-3-methylbenzopyrylium salts (HEILBRON and ZAKI), 1905.
7-Methoxy-4-phenyl-2:3-dimethylbenzopyrylium salts (HEILBRON and ZAKI), 1904.
7-Methoxy-4-phenyl-2-*p*-hydroxy-*m*-methoxystyryl-3-methylbenzopyrylium salts (HEILBRON and ZAKI), 1905.
7-Methoxy-4-phenyl-2-*p*-hydroxystyryl-3-methylbenzopyrylium salts (HEILBRON and ZAKI), 1904.
3-Methoxy-2-phenylindole (ROBINSON and THORNLEY), 3144.
7-Methoxy-4-phenyl-2-*p*-methoxystyryl-3-methylbenzopyrylium salts (HEILBRON and ZAKI), 1904.
2-Methoxyphenylmethyl sulphoxide, and 5-nitro- (POLLARD and ROBINSON), 3091.
2-Methoxyphenylmethyl sulphoxide, 4-nitro- (HOLMES, C. K. and E. H. INGOLD), 1689.
2-Methoxyphenylmethylsulphones, nitro- (HOLMES, C. K. and E. H. INGOLD), 1687.
4-Methoxyphthalidecarboxylic acid, 3-hydroxy- (PERKIN and TRIKOJUS), 2928.
2′-Methoxystyryl benzyl ketone (DICKINSON), 2238.
4′-Methoxy-2-styryl*iso*flavone, 5:7-*di*hydroxy-, and its diacetyl derivative (BAKER and ROBINSON), 2718.
Methoxy-9-styrylxanthylium salts, and their hydroxy-derivatives (ATKINSON and HEILBRON), 681.
5-Methoxythioanisoles, 2- and 4-nitro- (HODGSON and HANDLEY), 544.
3-Methoxytoluene, 2:4-*di*nitro- (GORNALL and ROBINSON), 1984.
3-Methoxy-*o*-toluidines, chloro-, and their acetyl derivatives (GIBSON), 1426.
Methoxytolyltelluri*tri*chlorides (MORGAN and KELLETT), 1086.
β-Methoxy*iso*valeric acid (FARMER and KRACOVSKI), 2321.
Methyl alcohol, viscosity and density of, and of solutions of electrolytes in it (EWART and RAIKES), 1907.
equilibrium between methyl formate and (CHRISTIANSEN), 413.
influence of dissolved salts on miscibility temperatures of mixtures of paraffins with (HOWARD and PATTERSON), 2787.
Methyl methylfructoside (ALLPRESS), 1722.
2-Methylacenaphthpyridine, and its salts, and 4-hydroxy- (NAIR and SIMONSEN), 3141.
4-Methylacenaphthpyridine, 2-chloro-, and 2-hydroxy- and its hydrochloride (NAIR and SIMONSEN), 3143.
***N*-Methylaceto-*o*-anisidide**, and its nitro-derivatives (C. K. and E. H. INGOLD), 1323.
1-Methylaminobenzthiazole, and its bromides (HUNTER), 1393, 2954.
1-Methylaminobenzthiazole, 5-bromo-, and its hexabromide (HUNTER and SOYKA), 2961.
4-Methylaminodiphenyl, derivatives of (BELL, KENYON, and ROBINSON), 1245.
4-Methylaminodiphenyl, *di*nitro-, and *di*nitro-4-nitroso- (BELL and KENYON), 2710.
6′-Methylaminodiphenylarsinic acid, 2-bromo- (BURTON and GIBSON), 458.
2-Methylamino-β-naphthathiazole, and its hexabromide (DYSON, HUNTER, and SOYKA), 2966.
***N*-Methyl-*o*-aminophenol**, *ON*-diacetyl derivative (C. K. and E. H. INGOLD), 1327.
p-toluenesulphonyl derivative (HEWITT, KING, and MURCH), 1368.
4-Methylaminophenylarsinic acid, and its toluenesulphonyl derivative, and its amino- and nitro-derivatives (HEWITT, KING, and MURCH), 1360.
4′-Methylanilinodiphenyl, bromo- and chloro-*di*nitro- (LE FÈVRE and TURNER), 2047.
4-Methylanilino-2-phenyldimethylpyrimidinium iodide (FORSYTH and PYMAN), 2509.
δ-Methylanilinosemicarbazide hydrochloride (BAIRD and WILSON), 2373.
***N*-Methyl-*o*-anisidines**, nitro- (C. K. and E. H. INGOLD), 1325.
***N*-Methylbenzaldoxime**, derivatives of (BRADY, DUNN, and GOLDSTEIN), 2394.
2-Methylbenzophenanthrazine, 1:3-*di*chloro- and 1:3:4-*tri*chloro- (DAVIES and LEEPER), 1416.

1-Methylbenzoxazole methiodide and methoperchlorate (CLARK), 234.
Methylbenzthiazoles, 1-amino-, and their bromides (HUNTER), 1398.
Methyl benzyl ketone δ-anilinosemicarbazone (BAIRD and WILSON), 2372.
Methyl *tert.*-**butyl ketone** δ-anilinosemicarbazone (BAIRD and WILSON), 2371.
9-Methylcarbazole, 3:6-*di*iodo- (TUCKER), 552.
N-**Methyl**-*p*-**chlorobenzaldoxime** (BRADY, DUNN, and GOLDSTEIN), 2391.
N-**Methylcinnamaldoxime**, and its hydriodide (BRADY, DUNN, and GOLDSTEIN), 2393.
d-**Methyldeoxybenzoin** (MCKENZIE, ROGER, and WILLS), 787.
Methyldeoxytetrahydro-α-methylmorphimethine, and its salts (CAHN), 2566.
Methyl-7:12-dihydrobenzophenarsazines, chloro- (BURTON and GIBSON), 2244.
2-Methyl-1:2-dihydrobenzthiazole, 1-imino-, and its bromides (HUNTER), 1392.
Methyldihydrodeoxytetrahydro-α-methylmorphimethine, and its salts (CAHN), 2568.
Methyldihydronaphtha*iso***quinolines**, and their picrates (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2257.
2-Methyl-5:10-dihydrophenarsazine, 10-chloro-, and its 5-acetyl derivative (BURTON and GIBSON), 468.
Methyldihydrothebainonemethine, and its salts and derivatives (CAHN), 2569.
N-**Methyl-3:4-dimethoxybenzaldoxime** (BRADY, DUNN, and GOLDSTEIN), 2391.
dl-**4-Methyldiphenyl** sulphoxide, 4′-amino-, preparation and resolution of, and its derivatives (HARRISON, KENYON, and PHILLIPS), 2085.
Methylene-blue, fixation of, by dispersoids (FODOR and RIWLIN), 102.
by yeast phosphoprotein sols (RIWLIN), 2300.
d-**Methylenecamphor**-*l*-**alanine**, ethyl ester (KIPPING and POPE), 496.
2:3-Methylenedioxybenzaldehyde. See *o*-Piperonal.
2:3-Methylenedioxybenzenylamino-oxime (PERKIN and TRIKOJUS), 2930.
2:3-Methylenedioxybenzoic acid. See *o*-Piperonylic acid.
3:4-Methylenedioxybenzomethylamide (BRADY and DUNN), 2415.
2:3-Methylenedioxycinnamic acid (PERKIN and TRIKOJUS), 2932.
3:4-Methylenedioxycinnamic acid, 6-bromo-, and its methyl ester (HAWORTH, PERKIN, and STEVENS), 1766.
6:7-Methylenedioxy-3(3′:4′-dimethoxybenzoyl)*iso***quinoline**, and its sulphate and oxime (CAMPBELL, HAWORTH, and PERKIN), 40.
6:7-Methylenedioxy-3-(3′:4′-dimethoxybenzoyl)1:2:3:4-tetrahydro*iso***quinoline**, and its salts and derivatives (CAMPBELL, HAWORTH, and PERKIN), 39.
6:7-Methylenedioxy-3-(3′:4′-dimethoxybenzyl)*iso***quinoline**, and its picrate (CAMPBELL, HAWORTH, and PERKIN), 41.
6:7-Methylenedioxy-3(3′:4′-dimethoxybenzyl)-1:2:3:4-tetrahydro*iso***quinoline**, and its salts (CAMPBELL, HAWORTH, and PERKIN), 41.
2:3-Methylenedioxy-11:12-dimethoxy-6:17- or **-6:15-dihydroparaberine**, and its salts (CAMPBELL, HAWORTH, and PERKIN), 42.
2:3-Methylenedioxy-11:12-dimethoxy-6:15:16:17-tetrahydroparaberine, and its salts (CAMPBELL, HAWORTH, and PERKIN), 41.
3:4-Methylenedioxyhomophthalic acid, preparation of, and its anhydride, and 4-bromo- (HAWORTH, PERKIN, and STEVENS), 1764.
6:7-Methylenedioxy-1-hydrindone, 4-bromo-, and its derivatives (HAWORTH, PERKIN, and STEVENS), 1767.
6:7-Methylenedioxy-3-(α-hydroxy-3′:4′-dimethoxybenzyl)*iso***quinoline**, and its picrate (CAMPBELL, HAWORTH, and PERKIN), 40.
6:7-Methylenedioxy-3-methylquinoline, and its salts (WILLIMOTT and SIMPSON), 2809.
3:4-Methylenedioxyphthalide (PERKIN and TRIKOJUS), 2930.
3:4-Methylenedioxystyrene, 6:α-*di*bromo- (HAWORTH, PERKIN, and STEVENS), 1766.
3:4′-Methylenedioxy-9-styrylxanthylium chloride (ATKINSON and HEILBRON), 682.
4′:5′-Methylenedioxy-9-styrylxanthylium chloride, 3:6-*di*hydroxy- (ATKINSON and HEILBRON), 683.
Methyl ethyl ketone, equilibrium of, with sodium iodide (WADSWORTH and DAWSON), 2784.

5-Methyl-2-ethyl-2-*iso*propenyl*cyclo*hexanone semicarbazone (KON and NUTLAND), 3110.

5-Methyl-2-ethyl-2-*iso*propenyl*cyclo*pentanone, and its semicarbazone (KON and NUTLAND), 3109.

2-Methyl*iso*flavone, 5:7-4′-*tri*hydroxy-. See 2-Methylgenistein.

5-Methylflavylium chloride, 3:7:3′:4′-*tetra*hydroxy- (ROBERTSON and ROBINSON), 1955.

Methylfructose, transformation of, into derivatives of γ-fructose (ALLPRESS), 1720.

2-Methylgenistein, and its derivatives (BAKER and ROBINSON), 2716.

Methylgenistein dimethyl ether, synthesis of (BAKER and ROBINSON), 2713.

β-Methylglutarimide-β-butyric acid, synthesis of (FARMER and ROSS), 3239.

1-Methylglyoxaline, 4-nitro-5-hydroxy-, and its salts (BALABAN), 571.

1-Methyl-Δ$^{1:3}$-*cyclo*hexadienyl-3-cyanoacetic acid, methyl esters, isomeric, and their dibromides (FARMER and ROSS), 1575.

1-Methyl-Δ$^{1:3}$-*cyclo*hexadienyl-3-α-cyanopropionic acid, methyl ester (FARMER and ROSS), 1576.

1-Methyl-Δ$^{1:3}$-*cyclo*hexadienyl-3-propionitrile (FARMER and ROSS), 1576.

6-Methylhexahydrocarbazole, 10:11-*di*hydroxy-, acetyl derivatives (MANJUNATH and PLANT), 2261.

Methyl*cyclo*hexanols, isomerism of, and their esters (GOUGH, HUNTER, and KENYON), 2052.

1-Methyl*cyclo*hexan-2-one δ-anilinosemicarbazone and phenylhydrazone (BAIRD and WILSON), 2372.

1-Methyl*cyclo*hexan-3-one-1-cyanoacetic acid, and its esters, and their semicarbazones (FARMER and ROSS), 3237.

1-Methyl*cyclo*hexan-3-one-1-malonamic acid (FARMER and ROSS), 3239.

1-Methyl-Δ^{1}-*cyclo*hexene-3:3-*di*cyanoacet-amide and -imide, and the ammonium salt of the latter (FARMER and ROSS), 1577.

α-Methyl-Δ^{1}-*cyclo*hexenylacetone semicarbazone (KON and SMITH), 1796.

2-Methyl-2-Δ^{1}-*cyclo*hexenyl*cyclo*hexanone, and its semicarbazone (KON and NUTLAND), 3105.

1-Methyl-Δ^{1}-*cyclo*hexenylidene-3-cyanoacetic acid (FARMER and ROSS), 3237.

salts and esters (FARMER and ROSS), 1574.

Methyl*cyclo*hexylcarbinol, resolution of (DOMLEO and KENYON), 1841.

β-Methylhydroxylamine, determination of (BRADY and GOLDSTEIN), 2407.

Methylmaltoside, and its derivatives (IRVINE and BLACK), 874.

Methylmethoxybenzaldoximes, and their derivatives (BRADY, DUNN, and GOLDSTEIN), 2391.

Methyl-3:4-methylenedioxybenzaldoximes, and their derivatives, and 6-nitro- and their hydrochlorides (BRADY, DUNN, and GOLDSTEIN), 2389.

Methylnaphthylquinolines, bromo-, chloro-, and nitro-, and their derivatives (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2252.

***N*-Methyl-2:4-*di*nitrobenzaldoxime** (BRADY, DUNN, and GOLDSTEIN), 2393.

***N*-Methylnitrobenzaldoximes**, derivatives of (BRADY, DUNN, and GOLDSTEIN), 2394.

Methyloctahydroacridines (PERKIN and SEDGWICK), 444.

2-Methylphenarsazinic acid, and its sodium salt and hydrochloride (BURTON and GIBSON), 469.

β-Methylpimelic-β-acetic acid, and its amide (FARMER and ROSS), 3239.

Methyl*iso*propylbenzaldehydes, iodo-4-hydroxy- (HENRY and SHARP), 2439.

Methylprunetol. See Methylgenistein.

2-Methylquinoline, and its alkiodides, condensations of (HUMPHRIES), 375; (TAYLOR and WOODHOUSE), 2971.

2-Methylquinoline, ω-bromo-, bromonitro-, and ω-hydroxy-derivatives (HAMMICK), 1302

3-Methylquinoline, preparation of, and its salts (WILLIMOTT and SIMPSON), 2809.

1-Methyl-2-quinolone-4-carboxylic acid, and its methyl ester (AESCHLIMANN), 2908.

***m*- and *p*-Methylstyrenes** (TITLEY), 517.

Methyl-1:2:3:4-tetrahydroacenaphthpyridines, and their salts and derivatives (NAIR and SIMONSEN), 3141.

6(or 8)-Methyltetrahydroacridine, and its picrate (PERKIN and SEDGWICK), 443.

6(or 8)-Methyltetrahydroacridinecarboxylic acid (PERKIN and SEDGWICK), 444.

***As*-Methyltetrahydroarsinoline**, derivatives of (ROBERTS, TURNER, and BURY), 1444.

6-Methyltetrahydrocarbazole, acetyl and benzoyl derivatives, and their derivatives (MANJUNATH and PLANT), 2261.

6-Methyltetrahydrocarbazolenine, 10- and 11-hydroxy-, and their acetyl derivatives (MANJUNATH and PLANT), 2262.

6-Methyltetrahydrocarbazyl-9-magnesium iodide (MANJUNATH and PLANT), 2263.

Methyl-1:2:3:4-tetrahydronaphthaquinolines, and their derivatives (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2252.

***S*-Methylthioguaiacol**, and 3:5-*di*bromo- and 5-nitro- (HOLMES, C. K. and E. H. INGOLD), 1687.

nitration of (POLLARD and ROBINSON), 3090; (C. K. and E. H. INGOLD), 3093.

Methylthiol groups, influence of, on colours (HODGSON and HANDLEY), 542.

γ-Methylxyloside (HAWORTH and WESTGARTH), 882.

Michler's hydrol, condensations with (HUMPHRIES), 375.

Micro-balance, studies with (HARTUNG), 840, 1349.

Molybdenum, position of, in the potential series (RUSSELL and ROWELL), 1881.

Molybdenum compounds, tervalent (WARDLAW and HARDING), 1592.

Molybdenum bromides (WARDLAW and HARDING), 1592.

Monosaccharides, constitution of (HIRST and MACBETH), 22; (HIRST), 350.

Morinidin chloride 3-methyl ether (GATEWOOD and ROBINSON), 1962.

Morphine derivatives, degradation of (CAHN), 2562.

*iso-apo***Morphine** dimethyl ether methosulphate (ROBINSON and SHINODA), 1994.

Morphine group (VAN DUIN, ROBINSON, and SMITH), 903; (CAHN and ROBINSON), 908.

Mother-of-pearl, formation of (GANGULY), 1381.

Müller Lecture (SØRENSEN), 2995.

N.

Naphthalene, 2-nitro-, preparation of, and its 1-halogen derivatives (HODGSON and KILNER), 7.

Naphthalene-4 sulphinic acid, 1-amino-, acetyl derivative (CHILD and SMILES), 2701.

α- and **β-Naphthanilides** (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2257.

Naphthaquinolines, derivatives of (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2247.

α- and **β-Naphthathiazoles**, 2-amino-, and their tetrabromides (HUNTER), 1400.

Naphthathioxins, synthesis of (CHILD and SMILES), 957.

β-Naphthoic acid, nitration of (HARRISON and ROYLE), 84.

α- and **β-Naphthoic acids**, amino-, and nitro-, and their salts and derivatives (HARRISON and ROYLE), 87.

β-Naphthol, 1-nitroso-, benzenesulphonyl derivative (EDWARDS), 815.

β-Naphthol-1-sulphonic acid, reaction of diazosulphonates from (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 690.

Naphthyl 4-*di*sulphoxide, 1-amino-, acetyl derivative (CHILD and SMILES), 2701.

Naphthylamines, nitro- (HODGSON and KILNER), 7.

***s*-α-Naphthylamylthiocarbamides** (DYSON, HUNTER, and SOYKA), 2968.

β-1-Naphthylaminocrotono-1-naphthylamide (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2252.

***s*-α-Naphthylbutylthiocarbamides** (DYSON, HUNTER, and SOYKA), 2967.

1-α-Naphthyl-2:2-dibenzylethylene glycol (MCKENZIE and DENNLER), 1601.

1-α-Naphthyl-2:2-dimethylethylene glycol (MCKENZIE and DENNLER), 1601.

1-α-Naphthyl-2:2-diphenylethylene glycol (MCKENZIE and DENNLER), 1601.

α-Naphthylglycollic acid, and its amide and methyl ester (MCKENZIE and DENNLER), 1599.

***s*-α-Naphthyl-*n*-heptylthiocarbamide** (DYSON, HUNTER, and SOYKA), 2969.

***s*-α-Naphthyl-*n*-hexylthiocarbamide** (DYSON, HUNTER, and SOYKA), 2969.

***s*-α-Naphthyl-*n*-propylthiocarbamide** (DYSON, HUNTER, and SOYKA), 2967.

Naphthylsulphuric acids, potassium salts (BURKHARDT and LAPWORTH), 689.

1-β-Naphthylthiol-2 naphthol (BROOKER and SMILES), 1728.

Narcotine, oxidation of, by hydrogen peroxide (DRUMMOND and MCMILLAN), 2702.

oxide (DRUMMOND and MCMILLAN), 2704.

Neodymium, ultra-violet spectrum of (GARDINER), 1518.
Neopine, constitution of, and its derivatives (VAN DUIN, ROBINSON, and SMITH), 903.
Nickel, electro-deposition potential of (GLASSTONE), 2887.
periodic passivity of (HEDGES), 2878.
removal of, from amalgams (RUSSELL, EVANS, and ROWELL), 1872.
Nickel alloys with cobalt and iron, electro-deposition potentials of (GLASSTONE), 2897.
Nickel *per*oxide as catalyst (CHIRNOAGA), 1698.
sulphate, equilibrium of potassium sulphate, water, and (CAVEN and JOHNSTON), 2628.
Nickel organic compounds, complex, with oximes (TAYLOR and EWBANK), 2818.
with ethylenediaminobisacetylacetone (MORGAN and SMITH), 920.
with $\gamma\gamma'\gamma''$-triaminotripropylamine (MANN and POPE), 489.
with $\beta\beta''\beta'$-triaminotriethylamine (MANN and POPE), 482.
Nickel membranes. See under Membranes.
Nicotine bromoaurate and compound with acetylene tetrabromide (FULTON), 198.
Nitrogen, active (WILLEY and RIDEAL), 1804.
Nitrogen *mono*xide (*nitrous oxide*), synthesis of (CHAPMAN, GOODMAN, and SHEPHERD), 1404.
interaction of hydrogen and, on the surface of gold (HUTCHISON and HINSHELWOOD), 1556.
*di*oxide (*nitric oxide*), interaction of hydrogen and (HINSHELWOOD and GREEN), 730.
catalytic decomposition of, on platinum (GREEN and HINSHELWOOD), 1709.
*tetr*oxide, effect of drying on (SMITS, DE LIEFDE, SWART, and CLAASSEN), 2663.
Nitrosylsulphuric acid (ELLIOTT, KLEIST, WILKINS, and WEBB), 1219.
Normeconinecarboxylic acid, and its methyl ester (PERKIN and TRIKOJUS), 2927.

O.

Obituary notices:—
John Young Buchanan, 993.
Katharine A. Burke, 3244.
Giacomo Luigi Ciamician, 996.
Samuel Henry Davies, 1004.
Obituary notices:—
William Henry Deering, 1006.
James Grant, 3244.
Francis Robert Japp, 1008.
Francis Jones, 1020.
Edmund Knecht, 1021.
William Robert Lang, 1024.
William James Lewis, 3245.
Frank George Pope, 1025.
Charles Etty Potter, 1027.
Shigetake Sugiura, 3246.
Robert Llewellyn Taylor, 1029.
Sir Edward Thorpe, 1031.
Octahydroacridine, and its derivatives (PERKIN and SEDGWICK), 438.
Oleic acid, oxidation of, and its derivatives (HILDITCH), 1828.
potassium salt, equilibria of potassium chloride, water, and (MCBAIN and ELFORD), 421.
Opianylidene-*dl*-piperitone, and its calcium salt (EARL and READ), 2075.
Optical activity and polarity of substituent groups (RULE and SMITH), 553; (RULE and NUMBERS), 2116; (RULE and MITCHELL), 3202.
potential, determination of (READ and MCMATH), 2183.
inversion, Walden's (WARD), 1184.
superposition (PATTERSON, FULTON, and SEMPLE), 3224.
Optically active compounds, relation between rotation and relative configuration of (CLOUGH), 1674.
Organic compounds, relation between crystal structure and length of chain in (PIPER, MALKIN, and AUSTIN), 2310.
lability of halogens in (MACBETH, NUNAN, and TRAILL), 1248.
Organo-metallic compounds, cyclic (DREW), 223, 3054.
Oxalic acid, photochemical decomposition of aqueous solutions of (ALLMAND and REEVE), 2834.
manganous salt, hydrates of (CHAMBERLAIN, HUME, and TOPLEY), 2620.
sodium salt, reactions of, with salts of weak metallic bases (BRITTON), 269.
Oxidation, low temperature, at charcoal surfaces (RIDEAL and WRIGHT), 1813, 3182.
Oximes, structure and metallic compounds of (TAYLOR and EWBANK), 2818.
isomerism of (BRADY and GOLDSTEIN), 1918, 2403; (BRADY, DUNN, and GOLDSTEIN), 2386; (BRADY and DUNN), 2411.

10:10′-Oxy-5:10-dihydrophenarsazine (BURTON and GIBSON), 462.
Oxygen, adsorption of, by charcoal (RIDEAL and WRIGHT), 1813.
Ozone, thermal reactivity of, in presence of hydrogen (BELTON, GRIFFITH, and MCKEOWN), 3153.

P

Palladium organic compounds:—
with $\beta\beta'\beta''$-triaminotriethylamine (MANN and POPE), 482.
Palladous compounds with ethylenediaminobisacetylacetone (MORGAN and SMITH), 921.
Palmitic acid, propyl ester (FEAR and MENZIES, 938.
Palmitic acid, 9:10-*di*hydroxy- (HILDITCH), 1836.
β-Palmityl *di*chlorohydrin (WHITBY), 1460.
Paraberine, derivatives of (CAMPBELL, HAWORTH, and PERKIN), 32.
Paraffins, influence of dissolved salts on miscibility temperatures of mixtures of ethyl or methyl alcohol with (HOWARD and PATTERSON), 2787.
*cyclo***Paraffins**, structure of (WIGHTMAN), 2541.
Paraffin wax, non-acidic oxidation products of (FRANCIS and GAUNTLETT), 2377.
Passivity, periodic, of metals (HEDGES), 2878.
Pelargonidin chloride, synthesis of (NOLAN, PRATT, and ROBINSON), 1969.
5:7:3′:4′:5′-Pentamethoxyflavylium salts (GATEWOOD and ROBINSON), 1964.
*bicyclo***Pentane series**, tautomerism in (HASSELL and INGOLD), 1836.
1-*cyclo***Pentane-1′-carboxylyl-***p*-**toluidino***cyclo***pentane-1-carboxylic acid**, 1′-hydroxy-, lactone (OAKESHOTT and PLANT), 1212.
*cyclo***Pentane-1:2-dicarboxylic acid**, 2:3-*di*bromo- (HASSELL and INGOLD), 1469.
*cyclo***Pentanol-1:2-dicarboxylic acid**, and its silver salt and ethyl ester (HASSELL and INGOLD), 1468.
*cyclo***Pentanone-3-carboxylic acid**, ethyl ester, and its semicarbazone (INGOLD, SHOPPEE, and THORPE), 1486.
*cyclo***Pentanonedicarboxylic acid**, ethyl ester (INGOLD, SHOPPEE, and THORPE), 1486.
*cyclo***Pentene-1:2-dicarboxylic acids** (HASSELL and INGOLD), 1469.
α-Δ^1-*cyclo***Pentenylacetophenone**, and its derivatives (FARROW and KON), 2135.
*cyclo***Pentylidenemalonic acid**, and its ethyl ester and derivatives (KON and SPEIGHT), 2731.
2-*cyclo***Pentylidene***cyclo***pentanone**, and its derivatives (KON and NUTLAND), 3106.
Peonidin chloride, synthesis of (NOLAN, PRATT, and ROBINSON), 1968.
Petroleum, chemistry of (BIRCH and NORRIS), 2545.
Persian, aromatic hydrocarbons from (BIRCH and NORRIS), 2545.
Phenanthraquinone, 2:7- and 4:5-*di*nitro-, nitration of (CHRISTIE and KENNER), 470.
2:4:7-*tri*nitro-, and its quinoxaline derivative (CHRISTIE and KENNER), 473.
Phenanthrene, absorption spectrum of (CAPPER and MARSH), 724.
Phenazineazine (DUTT), 1180.
Phenazineazineazine (DUTT), 1180.
p-**Phenetidine** zincichloride (BANFIELD and KENYON), 1625.
Phenol, *o*-amino-, acetyl derivatives, nitration of (C. K. and E. H. INGOLD), 1320.
3-bromonitro-derivatives, and 3-chloro-2-nitro-, and their salts and derivatives (HODGSON and MOORE), 157.
3:5-*di*halogeno-derivatives, and their acetates and benzoates (HODGSON and WIGNALL), 2077.
Phenols, halogenation of (SOPER and SMITH), 1582.
nitrosation of (HODGSON and MOORE), 2036.
condensation of, with chloral (CHATTAWAY), 2720.
Phenols, amino- and nitroamino-, acetyl derivatives (HEWITT and KING), 822.
3-halogeno-5-amino-, 3-halogeno-5-nitro-, and 3:5-*di*halogeno-, and their derivatives (HODGSON and WIGNALL), 2077.
Phenolglutareins (DUTT), 1132.
Phenolsuccineins (DUTT), 1132.
Phenol-4-sulphonic acid, 3-bromo-2:5:6-*tri*nitro-, potassium salt (HODGSON and MOORE), 161.
Phenoxides, interaction of aliphatic esters and, in alcoholic solution (GYNGELL), 2484.
sodium, substituted, reactions of ethyl iodide with (GOLDSWORTHY), 1254.
Phenoxtellurine, and its salts, and 10:10-*di*chloro- (DREW), 230.
acetate and sulphates (DREW), 3069.
Phenoxtellurine, nitro-, *di*nitro-, nitrohydroxy-, and *di*nitrohydroxy-, nitrates (DREW), 3065.

Phenoxtellurone (DREW), 3069.
4′-Phenoxydiphenyl, bromo- and chloro-*di*nitro- (LE FÈVRE and TURNER), 2047.
4-Phenoxyphenol, 2-nitro- (LEA and ROBINSON), 412.
***o*-Phenoxyphenylmethylchloroarsine** (ROBERTS and TURNER), 1209.
***p*-Phenoxyphenyltelluri*tri*chloride** (DREW), 227.
Phenthiarsine, 10-chloro- (ROBERTS and TURNER), 1207.
Phenyl acetylacetonyl sulphides, *mono-* and *di*-chloro-, and *o*-nitro- (BROOKER and SMILES), 1726.
4-acetylaminonaphthyl *di*sulphide, 2:5-*di*bromo- (CHILD and SMILES), 2701.
1-Phenylacetylisatin (AESCHLIMANN), 2909.
Phenyl aminobenzyl ketones, amino-, and their acetyl derivatives (HARRISON), 1238.
***p*-Phenylaminophenylarsinic acid.** See Diphenylamine-*p*-arsinic acid.
Phenyl*iso*amylcarbamyl chloride (PRICE), 3231.
***s*-Phenyl-*n*-amylthiocarbamide** (HUNTER), 2956.
***s*-Phenylamylthiocarbamides**, *s*-*p*-bromo- (HUNTER and SOYKA), 2963.
9-Phenylanthracene, 10-bromo- (COOK), 2168.
10-Phenylanthraphenone (COOK), 2170.
Phenylarsenious oxide, 4-amino-, 4′-toluenesulphonyl derivative, 3′-*mono-* and 3:3′-*di*-amino- (HEWITT, KING, and MURCH), 1362.
o-bromo- (BURTON and GIBSON), 457.
5-iodo-3-amino-4-hydroxy-, acetyl derivative, and 5-iodo-3-nitro-4-hydroxy- (MACALLUM), 1647.
Phenylarsinic acid, 4-amino- and aminohydroxy-, benzene- and toluene-sulphonyl derivatives, and their amino- and nitro-derivatives (HEWITT, KING, and MURCH), 1360.
o-bromo-, preparation of (BURTON and GIBSON), 456.
5-iodo-3-amino-4-hydroxy-, and its salts and derivatives (MACALLUM), 1645.
Phenylarsinic acids, aminohydroxy-, and their arylamides (HEWITT and KING), 817.
5-Phenylazobenzene, 2-hydroxy- (BELL and KENYON), 3047.
1-Phenylbarbituric acid, and *mono-* and *di*-bromo-, and hydrazide of the monobromo-acid (MACBETH, NUNAN, and TRAILL), 1253.
2-Phenyl-1:3-benzdithiole, and its 2-oxide (HURTLEY and SMILES), 1827.
2-Phenyl-1:3-benzdithiole-1-sulphonium salts (HURTLEY and SMILES), 1827.
Phenylbenzidine, *N-o*-nitro- (TUCKER), 3034.
N-**Phenylbenziminophenyl** thioether (CHAPMAN), 2298.
1-Phenylbenzoxazole methiodide (CLARK), 235.
1-Phenylbenzthiazole, and 5-amino-, 5-bromo-, and 5-nitro-, and their bromides (HUNTER), 539.
5-Phenyl-1:2:3-benztriazole, 1-acetyl derivative (BELL and KENYON), 2709.
Phenylbenzylarsinic acid, *l*-menthylamine and strychnine salts (ROBERTS, TURNER, and BURY), 1447.
Phenyl αα-bis-2:5-*di*chlorophenylthiolbenzyl ketone (BROOKER and SMILES), 1727.
Phenylbromoacetic acid, action of water on (WARD), 1184.
β-Phenyl-Δ$^{\beta}$-butenoic acid, and its methyl ester (JOHNSON and KON), 2752.
γ-Phenyl-Δ$^{\beta}$-butenoic acid. See Styrylacetic acid.
Phenylbutylcarbamyl chlorides (PRICE), 3231.
δ-Phenyl-*n*-butyldimethylarsine, derivatives of (ROBERTS, TURNER, and BURY), 1445.
***s*-Phenyl-*n*-butylthiocarbamide** (HUNTER), 2955.
***s*-Phenylbutylthiocarbamides**, *s*-*p*-bromo- (HUNTER and SOYKA), 2962.
γ-Phenylbutyramide, α-cyano- (LINSTEAD and WILLIAMS), 2747.
Phenylchloroacetic acid, action of water on (WARD), 1184.
Phenyl α-5-chloro-2-methoxyphenylthiol-α-2:5-*di*chlorophenylthiolbenzyl ketone (BROOKER and SMILES), 1727.
α-Phenylcinnamamides, 3:4′-*di*nitro-, ster-oisomeric (HARRISON and WOOD), 1197.
α-Phenylcinnamic acids, 3:4′-*di*nitro-, stereoisomeric (HARRISON and WOOD), 1198.
piperidine salts (HARRISON and WOOD), 580.
10-Phenyl-9:10-dihydroanthraphenone (COOK), 2171.
α-Phenyldihydrocinnamonitrile, 3:4′-*di*nitro-β-hydroxy- (HARRISON and WOOD), 1197.
2-Phenyl-4:5-dihydroglyoxaline, 2-*m*-nitro-, salts of (FORSYTH, NIMKAR, and PYMAN), 805.

3-Phenyl-1:3-dihydrophthalazine-4-acetic acid, 1-hydroxy-3:4′-nitro-, and its salts and derivatives (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 700.

3-Phenyl-1:3-dihydrophthalazine 4-acetic-1-sulphonic acid, 4′-nitro- (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 699.

m- and *p*-**Phenylenediacetonitriles**, reduction of (TITLEY), 508.

o-**Phenylenethiocarbamide**, sodium salt (STEPHEN and WILSON), 2536.

s-**Phenylethylthiocarbamide**, *p*-bromo- (HUNTER and SOYKA), 2962.

α-**Phenyl-γ-ethyl-Δβ-** and **-Δγ-penten-α-ones**, and their derivatives (FARROW and KON), 2136.

β-**Phenylethylphthalimide** (ING and MANSKE), 2350.

2-Phenylglyoxaline, bromo- and bromonitro-derivatives, and their salts (FORSYTH, NIMKAR, and PYMAN), 804.

s-**Phenyl-*n*-heptylthiocarbamide** (HUNTER), 2957.

s-**Phenyl-*n*-heptylthiocarbamide**, *s*-*p*-bromo- (HUNTER and SOYKA), 2964.

β-**Phenyl-Δβ-hexenoic acid**, and its derivatives (JOHNSON and KON), 2755.

Phenylhexenones, isomeric, and their derivatives (JOHNSON and KON), 2758.

s-**Phenyl-*n*-hexylthiocarbamide** (HUNTER), 2957.

s-**Phenyl-*n*-hexylthiocarbamide**, *s*-*p*-bromo- (HUNTER and SOYKA), 2964.

Phenyl *p*-hydroxybenzyl ketone, 2:4:6-*tri*hydroxy- (BAKER and ROBINSON), 2716.

β-**Phenylhydroxylamine**, condensation of acetone with (BANFIELD and KENYON), 1612.

N-**Phenyliminoisocarbostyril-3-carboxylic acid**, *N*-4′-nitro- (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 705.

4-Phenylimino-2-phenyldimethyldihydropyrimidine (FORSYTH and PYMAN), 2508.

Phenyl-*p*-methoxybenzyl ketone, 2:4:6-*tri*hydroxy- (BAKER and ROBINSON), 2717.

α-**Phenyl-2-methoxystyryl methyl ketone** (DICKINSON), 2238.

2-Phenyl-6-methyl-4-anilinopyrimidine, salts and derivatives of (FORSYTH and PYMAN), 2507.

2-Phenyl-2-methyl-1:3-benzdithiole (HURTLEY and SMILES), 1827.

β-**Phenyl-*α*-methylhydracrylaldehyde**, *β*-*o*-nitro- (WILLIMOTT and SIMPSON), 2308.

2-Phenyl-6-methyl-4-methylanilinopyrimidine, salts of (FORSYTH and PYMAN), 2509.

3-Phenylmethylmethyleneamino-2:4-diketotetrahydrothiazole 2-phenylmethylmethylenehydrazone (STEPHEN and WILSON), 2537.

β-**Phenyl-γ-methyl-Δβ-pentenoic acid**, and its derivatives (JOHNSON and KON), 2756.

Phenylmethylsulphone, *p*-amino-, acetyl derivative (CHILD and SMILES), 2699.

5-nitro-2-hydroxy-, and 3:5-*di*nitro-2-hydroxy- (POLLARD and ROBINSON), 3092.

s-**Phenylmethylthiocarbamide**, *p*-bromo- (HUNTER and SOYKA), 2961.

Phenyl nitrobenzyl ketones, nitro- (HARRISON and WOOD), 581.

Phenylnitromethanes, preparation and nitration of (BAKER and INGOLD), 2467.

Phenylnitrosoamine, *p*-nitro-, condensations with (HUMPHRIES), 375.

β-**Phenyl-Δβ-pentenoic acid**, and its derivatives (JOHNSON and KON), 2753.

δ-**Phenyl-Δγ-penten-β-one**, and its semicarbazone (JOHNSON and KON), 2757.

Phenyl-*β*-phenylethylmethylarsine, and its methiodide (ROBERTS, TURNER, and BURY), 1446.

3-Phenylphthalaz-4-one, 4′-amino-, and its derivatives (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 703.

N-**Phenylphthalimidine**, and 4-amino- and 4-hydroxy-, and their derivatives (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 704.

β-**Phenylpropionic acid**, *o*-cyano- (EDWARDS), 816.

β-**Phenylpropionic acids**, *α*-amino-*β*-hydroxy-. See Phenylserines.

Phenylpropylcarbamyl chlorides (PRICE), 3230.

γ-**Phenylpropyldimethylethylarsonium iodide** (ROBERTS, TURNER, and BURY), 1444.

s-**Phenyl-*n*-propylthiocarbamide**, *s*-*p*-bromo- (HUNTER and SOYKA), 2962.

Phenylpyridines, amino- and nitro-, and their salts (FORSYTH and PYMAN), 2916.

3-Phenyl-2-quinolone-4-carboxylic acid, 6-iodo- (AESCHLIMANN), 2911.

Phenylserines, isomeric, and their derivatives (FORSTER and RAO), 1943.

Phenylsuccinic acid, 5-iodo-2-amino- (AESCHLIMANN), 2911.

3-Phenyltetrahydrophthalazine-4-acetic acid, 1-hydroxy-3:4′-amino-, and its acetyl derivative (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 702.

Phenylthiocarbamides, *di-* and *tri*chloro- (DYSON, GEORGE, and HUNTER), 3042.
Phenylthiocarbimides, *di-* and *tri*chloro- (DYSON, GEORGE, and HUNTER), 3042.
o-**Phenylthiolphenylarsenious oxide** (ROBERTS and TURNER), 1208.
o-**Phenylthiolphenylarsinic acid** (ROBERTS and TURNER), 1208.
o-**Phenylthiolphenyl*di*chloroarsine** (ROBERTS and TURNER), 1208.
β-**Phenylvalerolactone** (JOHNSON and KON), 2755.
*iso***Phorone**, reactions of, and bromo- (BAKER), 663.
Phosphinic acids, formation of, from triarylmethoxyphosphorus dichlorides (BOYD and SMITH), 2323.
Phosphorus, inhibition of the glow of (EMELÉUS), 1336.
action of, on silver and other metallic salts (WALKER), 1370.
Phosphorus *pent*oxide, purification of (FINCH and FRASER), 117.
Phosphoric acid, conductivity of, at 0° (CAMPBELL), 3021.
Photochemical change, variation of the rate of, with intensity of light (BRIERS, CHAPMAN, and WALTERS), 562.
Photographic emulsions, analysis of (CLARK), 773.
Phthalbromomethylimide (BALABAN), 572.
Phthalide-acetamide and **-acetonitrile** (EDWARDS), 816.
Phthalidecarboxylic acid, 3:4-*di*hydroxy-. See Normeconinecarboxylic acid.
Phthalimidomethanesulphonic acid, and its barium salt (BALABAN), 573.
Phthalylbenzidine, derivatives of (LE FÈVRE and TURNER), 2482.
α-**Picoline**, and its methiodide, condensations of (HUMPHRIES), 375.
compound of acetylene tetrabromide and (FULTON), 199.
Picryl chloride, reaction of pyridine with, in alcoholic solution (HODGES), 2417.
4′-Piperazinodiphenyl, bromo- and chloro-*di*nitro- (LE FÈVRE and TURNER), 2048.
Piperidinodiphenyls, *tri*nitro-, and bromonitro- (LE FÈVRE and TURNER), 2044.
Piperitone, condensation of, with aldehydes (EARL and READ), 2072.
o-**Piperonal**, and its derivatives (PERKIN and TRIKOJUS), 2931.
ω-**Piperonoylacetophenone**, and its copper derivative (BRADLEY and ROBINSON), 2363.
Piperonoyl-α-furylcarbinyl benzoate (GREENE), 335.
Piperonyl ethyl ether (EDWARDS), 743.
o-**Piperonylic acid**, and its derivatives (PERKIN and TRIKOJUS), 2929.
N-*β*-**Piperonylethyl-3:4-methylenedioxyhomophthalamic acid**, and its methyl ester (HAWORTH and PERKIN), 1780.
N-*β*-**Piperonylethyl-3:4-methylenedioxyhomophthalimide** (HAWORTH and PERKIN), 1779.
Piperonylidenecyanoacetic acid, 6-bromo- (BAKER), 1075.
Piperonylidene-*dl*-piperitone (EARL and READ), 2075.
β-**Piperonylpropionamide**, *β*-6-bromo- (BAKER), 1075.
β-**Piperonylpropionic acid**, 6-bromo-, and its methyl ester (HAWORTH, PERKIN, and STEVENS), 1766.
β-**Piperonylpropionitrile**, *β*-6-bromo- (BAKER), 1075.
Piperonylpyruvic acid, oxime of (EDWARDS), 744.
Piperylenedicarboxylic acid (HASSELL and INGOLD), 1468.
Platinum, adsorption of water vapour on (LENHER), 1785.
Platinum anodes. See under Anodes.
Polarity and optical activity of substituent groups (RULE and SMITH), 553; (RULE and NUMBERS), 2116; (RULE and MITCHELL), 3202.
Polycyclic compounds, chemistry of, in relation to their homocyclic unsaturated isomerides (BAKER), 663; (HASSELL and INGOLD), 1836.
Polysaccharides, constitution of (IRVINE and ROBERTSON), 1488; (IRVINE and MACDONALD), 1502.
Potassium chloride, equilibria of potassium oleate, water, and (MCBAIN and ELFORD), 421.
halides, viscosity and density of methyl alcoholic solutions of (EWART and RAIKES), 1907.
equilibria of lead halides, water, and (BURRAGE), 1703.
*per*manganate, action of hydrogen peroxide on neutral solutions of (DUNNICLIFF and NIJHAWAN), 1.
nitrate and sulphate, equilibria of, in systems with sodium nitrate and sulphate (HAMID), 199, 206.
sulphate, equilibria of, with manganese, nickel, and zinc sulphates and water (CAVEN and JOHNSTON), 2628.
Potential at liquid junctions (CARTER and LEA), 834.

Praseodymium, ultra-violet spectrum of (GARDINER), 1518.
Precipitates, studies of (LAMBERT and HUME-ROTHERY), 2637; (LAMBERT and SCHAFFER), 2648.
Promoters, effect of, on catalytic oxidation by charcoal (RIDEAL and WRIGHT), 1813.
Propane, $\alpha\beta\gamma$-*tri*amino-, metallic complexes of, and its dihydrochloride hydriodide (MANN and POPE), 2675; (MANN), 2681.
Propane-$^{1:3}$‖$^{2:4}$-6-keto-4-methyl-3:4:5:6-tetrahydropyridine-5-carboxylic acid, and bromo- (FARMER and ROSS), 3238.
Propionic acid, β-thiol-, methyl ester of, and metallic derivatives (DRUMMOND and GIBSON), 3076.
p-iso-**Propoxyacetophenone** (BRADLEY and ROBINSON), 2362.
2-Propoxyanisole, nitro-derivatives (ALLAN and ROBINSON), 380.
4-Propoxyanisole, nitro-derivatives (ROBINSON and SMITH), 397.
p-iso-**Propoxybenzoic acid** (BRADLEY and ROBINSON), 2361.
ω-**4-*iso*-Propoxybenzoylacetophenone**, and its copper derivative (BRADLEY and ROBINSON), 2362.
1-*n*-Propylaminobenzthiazole, and its bromides (HUNTER), 2955.
1-*n*-Propylaminobenzthiazole, 5-bromo-, and its dibromide (HUNTER and SOYKA), 2962.
2-*n*-Propylamino-β-naphthathiazole, and its hexabromide (DYSON, HUNTER, and SOYKA), 2967.
N-*n*-**Propyl-*o*-benzoicsulphinide** (MCCLELLAND and GAIT), 924.
9-*iso*-Propylcarbazole, 3-iodo- (TUCKER), 553.
β-Propylcinnamic acids, derivatives of (JOHNSON and KON), 2755.
Propyl-Δ^1-*cyclo*hexenylacetone semicarbazone (KON and SMITH), 1796.
Propyl-1:2:4-triazoles, amino-, and their derivatives (REILLY and DRUMM), 1729.
5-chloro- (REILLY and DRUMM), 1735.
3-Propyl-1:2:4-triazole-5-azoacetoacetic acids, ethyl esters (REILLY and DRUMM), 1737.
3-Propyl-1:2:4-triazole-5-azoacetylacetones (REILLY and DRUMM), 1736.
3-*iso*-Propyl-1:2:4-triazole-5-azo-β-naphthol (REILLY and DRUMM), 1736.
3-Propyl-1:2:4:-triazole-5-azo-β-naphthylamines (REILLY and DRUMM), 1736.
3-*n*-Propyl-1:2.4-triazole-5-*iso*diazohydroxide (REILLY and DRUMM), 1735.
3-*n*-Propyl-1:2-4-triazolyl-5-hydrazine, and its benzaldehydehydrazone (REILLY and DRUMM), 1734.
Protopine, synthesis of (HAWORTH and PERKIN), 1769.
Prunetol, constitution of, and its identity with genistein (BAKER and ROBINSON), 2713.
Pulegone, imide from condensation of ethyl sodiocyanoacetate and (KON and NUTLAND), 3110.
Pyridine, reaction between picryl chloride and, in alcoholic solution (HODGES), 2417.
equilibrium of sulphur and (HAMMICK and HOLT), 1995.
bromoaurate and compound with acetylene tetrabromide (FULTON), 198.
Pyrocatechol, crystal structure of (CASPARI), 573.
Pyrylium salts of anthocyanidin type (ROBERTSON and ROBINSON), 1951; (GATEWOOD and ROBINSON), 1959; (NOLAN, PRATT, and ROBINSON), 1968.

Q.

Quartz, adsorption of water on (LENHER), 1785.
Quercetin, synthesis of, and its derivatives (ALLAN and ROBINSON), 2334.
Quinaldine. See 2-Methylquinoline.
Quinizarin, action of thionyl chloride on (GREEN), 1428.
Quinol, crystal structure of (CASPARI), 2944.
Quinoline, equilibrium of sulphur and (HAMMICK and HOLT), 1995.
iso-**Quinoline derivatives**, syntheses of (CAMPBELL, HAWORTH, and PERKIN), 32.
n- and *iso*-**Quinolines**, bromoaurates and compounds with acetylene tetrabromide (FULTON), 198.
iso-**Quinoline alkaloids**, syntheses of (EDWARDS), 740, 813.
Quinoline-2-aldehyde, 8-nitro- (HAMMICK), 1304.
Quinolinocupric acetylacetone (MORGAN and SMITH), 919.
Quinolone compounds, relative stability of indolinone compounds and (AESCHLIMANN), 2902.
2-Quinolone-4-carboxylic acid, 6-iodo-, and its esters (AESCHLIMANN), 2910.
3-thiol-, quinoxaline derivative (AESCHLIMANN), 2909.

R.

Reactions, termolecular (COUTIE), 887.
Resins in coal (FRANCIS and WHEELER), 1410.
Resorcinol, 5-bromo-, 2:4:6-*tri*bromo-5-iodo-, 5-chloro-, 5-chloro-2:4:6-*tri*bromo-, and 5-iodo- (HODGSON and WIGNALL), 2827.
*iso*Rhamnetin, synthesis of, and its tetra-acetyl derivative (HEAP and ROBINSON), 2336.
Rhamnose, constitution of (HIRST and MACBETH), 22.
Ring compounds, influence of carbon rings in, on velocity of reactions involving side-chains (GANE and INGOLD), 10.
Rotatory power and chemical constitution (SINGH and PURI), 504; (HARRISON, KENYON, and SHEPHERD), 658; (DOMLEO and KENYON), 1841; (HARRISON, KENYON, and PHILLIPS), 2079.
relation between relative configurations of optically active compounds and (CLOUGH), 1674.
Rubber. See Caoutchouc.

S.

Sabinol, oxidation of, with hydrogen peroxide (HENDERSON and ROBERTSON), 2761.
Salicylaldehyde, condensation of, with benzyl methyl ketone (DICKINSON), 2234.
Salicylic acid, absorption spectra of salts and derivatives of (PURVIS), 775.
heat of combustion of (VERKADE and COOPS), 1437.
Salicylic acid, 5-nitro-, and its ethyl ester, crystallography of (CHATTAWAY and CURJEL), 3210.
Salicylidene-*dl*-piperitone (EARL and READ), 2074.
Salvarsan, synthesis of iodine derivatives of (MACALLUM), 1645.
Samarium, ultra-violet spectrum of (GARDINER), 1518.
Selenium, oxidation potential of (CARTER, BUTLER, and JAMES), 930.
Selenium *di*oxide, action of hydrofluoric acid on (PRIDEAUX and MILLOTT), 167.
Selenium organic compounds, aromatic (CHALLENGER, PETERS, and HALÉVY), 1648.
Selenocyanates (CHALLENGER, PETERS, and HALÉVY), 1654.
Selenocyanoaniline (CHALLENGER, PETERS, and HALÉVY), 1654.
Selenocyanodimethylaniline (CHALLENGER, PETERS, and HALÉVY), 1654.
Selenocyano-groups, introduction of, into aromatic compounds (CHALLENGER, PETERS, and HALÉVY), 1648.
Semicarbazones, action of hydrazines on (BAIRD and WILSON), 2367.
Sesquiterpenes, oxidation of, with chromyl chloride and chromic acid (GIBSON, ROBERTSON, and SWORD), 164.
Silicoethylene, *di*chloro-, *di*bromide (WIDDOWSON), 958.
Silicon, atomic weight of (ROBINSON and SMITH), 1262.
Silicon *tetra*chloride, density and coefficient of expansion of (ROBINSON and SMITH), 3152.
*di*oxide (*silica*) hydrated, interaction of, with neutral salts in relation to adsorption (MUKHERJEE, GHOSH, KRISHNAMURTI, GHOSH, MITRA, and ROY), 3023.
Silicon organic compounds (WIDDOWSON), 958.
Silver, atomic weight of (RILEY and BAKER), 2510.
Silver salts, action of phosphorus on (WALKER), 1370.
oxidation of tartaric acid by solutions of (MAXTED), 2178.
Silver germanate (PUGH), 2832.
iodide, photochemical decomposition of (HARTUNG), 1349.
Silver anodes. See under Anodes.
Soap, equilibria in processes of boiling (MCBAIN and ELFORD), 421.
solutions, concentration of electrolytes for salting out of (MCBAIN and PITTER), 893.
Sodium chloride and nitrate, equilibria of barium chloride and nitrate with (FINDLAY and CRUICKSHANK), 316.
germanate (PUGH), 2828.
halides, viscosity and density of methyl alcoholic solutions of (EWART and RAIKES), 1907.
hydroxide, equivalent conductivity of solutions of (RAIKES, YORKE, and EWART), 630.
hypochlorite, catalytic decomposition of solutions of, by finely divided metallic oxides (CHIRNOAGA), 1693.
hyposulphite, reduction of arsenic compounds by (FARMER and FIRTH), 119.
iodide, solubility of, in ethyl alcohol (KING and PARTINGTON), 20.
equilibria of, with acetone and with methyl ethyl ketone (WADSWORTH and DAWSON), 2784.

Sodium nitrate and sulphate, equilibria of, in systems with potassium nitrate and sulphate (HAMID), 199, 206.
sulphate, equilibrium of sodium sulphide, water, and (HOGG), 855.
equilibrium of sodium thiosulphate, water, and (GARRAN), 848.
sulphide, equilibrium of sodium sulphate, water, and (HOGG), 855.
thiosulphate, equilibrium of sodium sulphate, water, and (GARRAN), 848.
Solid state, complexity of (SMITS and SCHOENMAKER), 1108, 1603.
Solubility (GLASSTONE, DIMOND, and JONES), 2935; (GLASSTONE, DIMOND, and HARRIS), 2939.
of sparingly soluble compounds (MITCHELL), 1333.
Solvents, selective action of (WRIGHT), 1203.
Spectra, absorption, and tautomerism (MORTON and ROSNEY), 706; (MORTON and ROGERS), 713.
of condensed nuclear hydrocarbons (CAPPER and MARSH), 724.
Tesla-luminescence (MCVICKER, MARSH, and STEWART), 17.
Squalene, constitution of, and its identity with spinacene (HEILBRON, KAMM, and OWENS), 1630.
hydrogenation of, in presence of nickel (HEILBRON, HILDITCH, and KAMM), 3131.
Starch, structure of (IRVINE and MACDONALD), 1502.
Stearic acids, *di*hydroxy-, isomerism of (HILDITCH), 1828.
Stearolic acid, hydration of (G. M. and R. ROBINSON), 2204.
β-Stearyl *di*chlorohydrin (WHITBY), 1460.
Stilbene, derivatives of (ASHLEY), 2804.
Stilbene, *di*amino- and *di*nitro-derivatives, asymmetrically substituted (HARRISON), 1232.
α-chloro*di*nitro-, and 3:4′-*di*nitro-, and its *di*chloride (HARRISON and WOOD), 580.
Stilbene series, *as-di*amino- and *-di*nitro-derivatives (HARRISON and WOOD), 577.
Strontium sulphate, precipitated (LAMBERT and HUME-ROTHERY), 2637.
Styrylacetic acid, and its salts and derivatives, and α-cyano-, ethyl ester (LINSTEAD and WILLIAMS), 2741.
Styrylacetone, and its semicarbazone (LINSTEAD and WILLIAMS), 2744.
Styryl alkyl ketones, isomeric (MCGOOKIN and SINCLAIR), 1578.
Styrylbenzopyrylium salts (HEILBRON and ZAKI), 1902.
Styryl benzyl ketone, 2-hydroxy-, and its derivatives (DICKINSON), 2237.
Styryl 3:4-dimethoxyphenyl ketone, 2-hydroxy- (ROBERTSON and ROBINSON), 1952.
Styrylpyrylium salts (ATKINSON and HEILBRON), 676.
9-Styrylxanthylium chloride, 4′-*mono*- and 3:4′:6-*tri*- hydroxy- (ATKINSON and HEILBRON), 680.
Suberic acid, αα′-*di*bromo-, and its ethyl ester, and αα′-*di*hydroxy- (GOSS and INGOLD), 1473.
Substance, $C_{13}H_{13}O_3N_4I$, from α-picoline methiodide and *p*-nitrophenylnitrosoamine (HUMPHRIES), 376.
$C_{15}H_{24}O$, and its semicarbazone, from oxidation of cedrene (GIBSON, ROBERTSON, and SWORD), 166.
$C_{17}H_{15}O_2N_4I$, from quinaldine methiodide and *p*-nitrophenylnitrosoamine (HUMPHRIES), 376.
$C_{18}H_{22}O_3N_2$, and its derivatives, from acetone and β-phenylhydroxylamine (BANFIELD and KENYON), 1621.
$C_{19}H_{17}O_2N_4I$, from quinaldine ethiodide and *p*-nitrophenylnitrosoamine (HUMPHRIES), 376.
$C_{21}H_{14}O_2$, and its acetate, from benzylideneanthrone dibromide and silver oxide (COOK), 2171.
$C_{23}H_{27}N_3$, from α-picoline and Michler's hydrol (HUMPHRIES), 375.
$C_{26}H_{32}O$, from dehydration of 1-α-naphthyl-2:2-dibenzylethylene glycol (MCKENZIE and DENNLER), 1602.
$C_{27}H_{29}N_3$, and its oxalate, from quinaldine and Michler's hydrol (HUMPHRIES), 375.
$C_{28}H_{31}N_3$, from *p*-toluquinaldine and Michler's hydrol (HUMPHRIES), 375.
$C_{29}H_{34}N_3I$, from *p*-toluquinaldine methiodide and Michler's hydrol (HUMPHRIES), 375.
$C_{41}H_{36}O_4$, from benzyl methyl ketone and salicylaldehyde DICKINSON), 2239.
Substitution in aromatic compounds (DAVIES and LEEPER), 1413; (FLÜRSCHEIM and HOLMES), 1562.
directive power of groups in (ALLAN and ROBINSON), 376; (OXFORD and ROBINSON), 383; (ROBINSON and SMITH), 392; (ALLAN, OXFORD, ROBINSON, and SMITH), 401; (LEA and ROBINSON), 411.

Substitution in aromatic compounds, efficiency of oxygen and sulphur in (HOLMES, C. K. and E. H. INGOLD), 1684.
with reference to polar and non-polar dissociation (C. K. and E. H. INGOLD), 1310.
Sucrose, constitution of (MCOWAN), 1737, 1747; (HAWORTH and HIRST), 1858.
Sugars, classification of (MALTBY), 1629.
ring structure of (DREW and HAWORTH), 2305.
carbonates of (HAWORTH and MAW), 1751.
structure of lactones from (HAWORTH and NICHOLSON), 1899.
use of methyl alcohol as solvent for mutarotation of (FAULKNER and LOWRY), 1938.
Sulphoacetic acid, chloro-, resolution of, and its salts (READ and MCMATH), 2192.
3-Sulphobenzoic acid, 2:4-*di*nitro-, sodium salt (GORNALL and ROBINSON), 1983.
***p*-Sulphophenylarsenobenzene** (HEWITT, KING, and MURCH), 1370.
***p*-Sulphophenylarsinic acid** (HEWITT, KING, and MURCH), 1369.
Sulphoxides, resolution of (HARRISON, KENYON, and PHILLIPS), 2079.
Sulphur, equilibria of, with pyridine, quinoline, and *p*-xylene (HAMMICK and HOLT), 1995.
Sulphur *di*oxide, interaction of hydrogen sulphide and (MATTHEWS), 2270.
*tri*oxide, pure (SMITS and SCHOENMAKER), 1108, 1603.
Sulphuric acid, action of copper on (ROGERS), 254.
Thionyl bromide and chlorobromide (MAYES and PARTINGTON), 2594.
chloride, action of, on hydroxyanthraquinones (GREEN), 1428.
Supa oil, constituents of (HENDERSON, M'NAB, and ROBERTSON), 3077.

T.

Tagetes glandulifera, ketones from volatile oil of (JONES), 2767.
Tartaric acid, oxidation of, by silver salts in solution (MAXTED), 2178.
sodium salt, reactions of, with salts of weak metallic bases (BRITTON), 269.
Tautomerism, mechanism of (INGOLD, SHOPPEE and THORPE), 1477.
and absorption spectra (MORTON and ROSNEY), 706; (MORTON and ROGERS), 713.
Tautomerism and additive reactions (COOPER, C. K. and E. H. INGOLD), 1868.
ring-chain (DUTT), 1132.
three-carbon (KON), 1792; (FARROW and KON), 2128; (KON and SPEIGHT), 2727; (LINSTEAD and WILLIAMS), 2735; (JOHNSON and KON), 2748; (KON and NUTLAND), 3101.
Tellurium *tetra*chloride, reactions of, with aryl alkyl ethers (MORGAN and KELLETT), 1080.
*di*oxide, action of hydrogen fluoride on (PRIDEAUX and MILLOTT), 520.
Tellurium organic compounds, cyclic (DREW), 223.
Tellurylium compounds (DREW), 3054.
Telluripropionic acid, *tri*bromo-, and *tri*chloro- (MORGAN and KELLETT), 1087.
Tetra-acetylglucose, mutarotation of (JONES and LOWRY), 720.
Tetra*tri*aminopropanetricupric salts (MANN), 2685.
Tetrabromo(*tri*aminopropanehydrochloride)platinum hydrate (MANN), 2687.
Tetracarbethoxy-*l*-arabinose (HAWORTH and MAW), 1752.
Tetracarbethoxy-*l*-xylose (HAWORTH and MAW), 1754.
Tetracarbomethoxy-*l*-arabinose (HAWORTH and MAW), 1752.
Tetracarbomethoxy-*l*-xylose (HAWORTH and MAW), 1754.
Tetrachloro(*tri*aminopropanehydrochloride)platinum salts (MANN), 2686.
Tetrahydroacridine, and its derivatives (PERKIN and SEDGWICK), 438.
***As*-Tetrahydroarsinoline**, chloro- (ROBERTS, TURNER, and BURY), 1443.
Tetrahydrocarbazole, derivatives of (COLLAR and PLANT), 808; (MANJUNATH and PLANT), 2260.
Tetrahydrocarbazolecarboxylic acids, and their salts and derivatives (COLLAR and PLANT), 808.
α- and β-Tetrahydrodeoxycodeines, isomerism of (CAHN), 2572.
Tetrahydro*iso*phthalic acids, and their esters (FARMER and RICHARDSON), 2172.
2′:3′:5:6-Tetramethoxy-2-benzylidene-1-hydrindone (PERKIN, RÂY, and ROBINSON), 953.
Tetramethoxyflavylium ferrichlorides (ROBERTSON and ROBINSON), 1954.
Tetramethyladipic acids, electrolytic synthesis of (FARMER and KRACOVSKI), 2318.

3:3′-Tetramethyl*di*aminodiphenyl (DUTT), 1181.
3:6-Tetramethyl*di*amino-9-phenylfluorene, and its acetate (DUTT), 1181.
Tetramethylbenzidine, 2:2′-*di*amino-, 2-nitro-, and *di*nitro-, and their derivatives (BELL and KENYON), 2711.
Tetramethyl γ-fructose, oxidation of (MCOWAN), 1737.
Tetramethyl gluconolactones, and their phenylhydrazides (CHARLTON, HAWORTH, and PEAT), 99.
Tetramethylglucose, mutarotation of (JONES and LOWRY), 720; (FAULKNER and LOWRY), 1940.
oxidation of (HIRST), 351.
1:4:5:8-Tetramethylthianthren, and its disulphone (SEN and RÂY), 1140.
Tetra*cyclo*squalene, dehydrogenation of (HARVEY, HEILBRON, and KAMM), 3136.
Thallium compounds, use of, in organic chemistry (FEAR and MENZIES), 937.
Thallium *sub*oxide (AUFENAST and TERREY), 1546.
Thallous chloride, solubility of, in salt solutions, and its heats of solution (BUTLER and HISCOCKS), 2554.
Thianthren, *di*amino-, compounds of, with β-naphthol and with resorcinol (SEN and RÂY), 1141.
Thianthren series, synthesis in (SEN and RÂY), 1139.
Thianthren-2:6-bisdiazoaminobenzene-4′-sulphonic acid (SEN and RÂY), 1141.
Thiazole derivatives (STEPHEN and WILSON), 2531.
Thio-aryl groups, insertion of (BROOKER and SMILES), 1723.
Thiocarbonyl chloride, action of, on chloro-substituted anilines (DYSON, GEORGE, and HUNTER), 3041.
Thiocarbonylbenzidine, and its derivatives (LE FÈVRE and TURNER), 2483.
Thiocyanic acid, ammonium salt, action of light on aqueous solutions of (HOLMES), 1690; (WERNER and BAILEY), 2970.
Thionyl bromide and chloride. See under Sulphur.
2:3-Thionylanthragallol (GREEN), 2202.
1:2-Thionyl-7-chlorothionylanthrapurpurin (GREEN), 2200.
Thionylhystazarin (GREEN), 2201.
Thionylpurpurin (GREEN), 2200.
Thorium salts, reactions of, with sodium acetate and tartrate (BRITTON), 272.
Thyroxin, tautomerism of (HICKS), 643.
Tin organic compounds (LAW), 3243.
Tin anodes. See under Tin.
Titanium:—
Titanous sulphate, oxidation of, by air, and its prevention (RUSSELL), 497.
Tolane, *di*amino- and *di*nitro-derivatives, asymmetrically substituted (HARRISON), 1232.
3:4′-*di*amino-, and its diacetyl derivative, 3:4′-*di*nitro- (HARRISON), 1237.
Tolane series, *as*-*di*amino- and -*di*nitro-derivatives (HARRISON and WOOD), 577.
Toluene, 2:3:4-*tri*amino- and -*tri*nitro- (GORNALL and ROBINSON), 1981.
2-chloro-4-nitro-, chlorination of (DAVIES and LEEPER), 1413.
o-nitro-, mercuration of (COFFEY), 637; (BURTON, HAMMOND, and KENNER), 1802.
m- and *p*-nitro-, mercuration of (COFFEY), 3215.
Toluene-5-sulphinic acid, 2-amino-, acetyl derivative (CHILD and SMILES), 2700.
Toluenesulphinic acids, 2-nitro- (COFFEY), 642.
4-nitro-, and their salts (COFFEY), 3220.
p-**Toluenesulphonamides**, substituted, hydrolysis of (HOLMES and INGOLD), 1308.
p-**Toluenesulphonic acid**, beryllium salt (SIDGWICK and LEWIS), 1290.
4-Toluenesulphonic acid, 3-nitro-, salts of (HEWITT, KING, and MURCH), 1360.
Toluenesulphonic acids, 4-nitro-, and 4-nitro-2-amino-, and their salts (COFFEY), 3221.
Toluene-5-sulphonyl chloride, 2-amino-, acetyl derivative (CHILD and SMILES), 2700.
m-**Toluic acid**, ω-chloro-, ethyl ester (MORGAN and PORTER), 1258.
o-**Toluidine**, 3-bromo-, acetyl derivative (BURTON, HAMMOND, and KENNER), 1803.
m-**Toluidine**, 2:6-*di*chloro-4-nitro- (DAVIES and LEEPER), 1416.
1-*p*-**Toluidino-1-cyano*cyclo*pentane** (OAKESHOTT and PLANT), 1211.
1-*p*-**Toluidino*cyclo*pentane-1-carboxylic acid**, and its derivatives (OAKESHOTT and PLANT), 1210.
o-**Toluonitrile**, 6-bromo- (BURTON, HAMMOND, and KENNER), 1803.
p-**Toluoyl-2-methylquinoline**, and its methiodide, condensations of (HUMPHRIES), 375.

2:5-Toluquinone, halogen derivatives and their oximes (HODGSON and MOORE), 2036.

Toluthiazoles, ψ-amino-, hydrochlorides (HUNTER), 1397.

Tolyl mercaptan, sulphides and sulphoxides, 2-amino-, and their acetyl derivatives (CHILD and SMILES), 2700.

***m*-Tolyl** methyl ether, 2:6-*di*chloro-, and 6-chloro-2-nitro- (GIBSON), 1426.
6-*mono*- and 2:6-*di*-nitro-4-hydroxy-, acetyl derivatives (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1974.

***p*-Tolyl** acetylacetonyl sulphide (BROOKER and SMILES), 1726.
methyl ether, 3-hydroxy-, and 5-nitro-3-hydroxy-, acetyl derivatives, and 2-nitro-3-hydroxy- (GULLAND and ROBINSON), 1978.
selenocyanate (CHALLENGER, PETERS, and HALÉVY), 1654.

***N*-*p*-Tolylbenzimino-*p*-tolyl** thioether (CHAPMAN), 2298.

***m*-Tolylenediamine-3-sulphonic acid**, sodium salt and derivatives (GORNALL and ROBINSON), 1982.

β-*m*- and -*p*-Tolylethylamines, and their derivatives (TITLEY), 517.

***o*-Tolylethylcarbamyl** chloride (PRICE), 3231.

β-*m*- and -*p*-Tolylethylmethylamines, and their salts (TITLEY), 517.

***m*-Tolyl-α-naphthylamine**, 2:4-*di*nitro- (GORNALL and ROBINSON), 1984.

Tolyl 2-nitrotoluene-5-sulphazide, 2-nitro- (COFFEY), 642.

***m*-Tolylpiperidine**, 2:4-*di*nitro- (GORNALL and ROBINSON), 1984.

5-*p*-Tolylthiol-6-hydroxyquinoline (BROOKER and SMILES), 1728.

1-*p*-Tolylthiol-2-naphthol (BROOKER and SMILES), 1728.

α-*p*-Tolylthiolpropionic acid (BROOKER and SMILES), 1726.

3:4:5-Triacetoxy-ω-methoxyacetophenone (GATEWOOD and ROBINSON), 1965.

Triazans, reversible formation of (COOPER and INGOLD), 1894.

Tribenzylamine, *mm'm''-tri*nitro- (GOSS, INGOLD, and WILSON), 2457.

α- and ω-1:3:4-Tricarbethoxy-2-keto-*cyclo*pentylmethylsuccinic acids, ethyl esters (INGOLD and SHOPPÉE), 1916.

Triethylamine, *ββ'β''-tri*amino-, complex nickel and palladium salts of (MANN and POPE), 482.

Tri*cyclo*hexylarsine, derivatives of (ROBERTS, TURNER, and BURY), 1446.

3:4:3'-Trimethoxybenzophenone, and its oxime (LEA and ROBINSON), 2355.

3:4:5-Trimethoxybenzoylacetophenone, and its copper derivative (BRADLEY and ROBINSON), 2365.

3:3':4'-Trimethoxyflavone, 7-hydroxy-, 5:7-*di*hydroxy-, and their acetyl derivatives (ALLAN and ROBINSON), 2335.

5:7:4'-Trimethoxy-2-methyl*iso*flavone (BAKER and ROBINSON), 2718.

3:3':4'-Trimethoxy-5-methylflavylium ferrichloride, 7-hydroxy- (ROBERTSON and ROBINSON), 1955.

3:4:5-Trimethoxyphenyl 2-hydroxy-4:6-dimethoxystyryl ketone (GATEWOOD and ROBINSON), 1963.

Trimethyl γ arabonolactone, structure of (HAWORTH and NICHOLSON), 1899.

Trimethylenesilicon *di*chloride (WIDDOWSON), 958.

Trimethylglucose, new crystalline forms of (HAWORTH and SEDGWICK), 2573.

3:3:5-Trimethyl*cyclo*hexan-1-one, 1:3:4:5-*tetra*bromo- (BAKER), 668.

1:1':3:3:3':3'-Trimethyl*bicyclo*hexyl-5:5'-dione, and its disemicarbazone (BAKER), 669.

Trimethylnaphthalene picrate (BIRCH and NORRIS), 2553.

Triphenylstibine hydroxyselenocyanate (CHALLENGER, PETERS, and HALÉVY), 1653.

Trimethyl xylonolactones (HAWORTH and WESTGARTH), 885.

Trimethyl γ-xylose (HAWORTH and WESTGARTH), 885.

Triphenylmethane, *p*-hydroxy-*p'p''-di*amino- (DUTT), 1174.

Triphenylmethoxyphosphorus *di*chlorides, *p*-bromo-, *p*-chloro-, and *p*-nitro- (BOYD and SMITH), 2327.

9-Triphenylmethylanthrone, 9-hydroxy- (INGOLD and MARSHALL), 3087.

Triphenylmethylphosphinic acid, *p*-bromo-, *p*-chloro-, and *m*-hydroxy-, and their salts and derivatives (BOYD and SMITH), 2328.

2:4:6-Triphenylthiolphloroglucinol, chloro-derivatives (BROOKER and SMILES), 1727.

Triphthalimidotripropylamine, and its hydrobromide (MANN and POPE), 490.

Tripropylamine, *γγ'γ''-tri*amino-, and its salts and derivatives and complex compounds with nickel (MANN and POPE), 489.

Trithallium methylglucoside (FEAR and MENZIES), 939.

2:4:6-Tri-*p*-tolylthiolorcinol (BROOKER and SMILES), 1728.

2:4:6-Tri-*p*-tolylthiolphloroglucinol (BROOKER and SMILES), 1727.

2:4:6-Triphenylthiolresorcinol, chloro-derivatives (BROOKER and SMILES), 1728.
Trypanocidal action and chemical constitution (HEWITT and KING), 817; (HEWITT, KING, and MURCH), 1355.
Tungsten, position of, in the potential series (RUSSELL and ROWELL), 1881.

U.

Ultrafiltration, nickel membranes for (MANNING), 1127.
Unsaturated compounds, formation of, from halogenated open-chain derivatives (HASSELL and INGOLD), 1465; (GOSS and INGOLD), 1471.
orienting influence of free and bound ionic charges on simple or conjugated (ING and ROBINSON), 1655.
homocyclic, chemistry of polycyclic compounds in relation to isomeric (HASSELL and INGOLD), 1836.

V.

Valency (NORRISH and JONES), 55; (LOWRY and OWEN), 606; (LOWRY and SASS), 622.
Valine, *n*-butyl ester, and its hydrochloride and picrate (MORGAN), 83.
Vanadium:—
Vanadous sulphate as a reducing agent (RUSSELL), 497.
Vapour pressure of liquids, by a differential method (JOLLY and BRISCOE), 2154.
Veratric anhydride (ALLAN and ROBINSON), 2334.
Veratrole, 3- and 6-amino- and -nitro-derivatives, and their derivatives (OXFORD), 2004.
***N*-β-Veratrylethyl-3:4-methylenedioxyhomophthalamic acid**, and its methyl ester (HAWORTH and PERKIN), 1776.
***N*-β-Veratrylethylmethylenedioxyhomophthalimides** (HAWORTH and PERKIN), 1776.
2-Veratrylidene-4:6-dimethoxycoumaranone (PERKIN, RÂY, and ROBINSON), 951.
2-Veratrylidene-1-hydrindone (PERKIN, RÂY, and ROBINSON), 951.
Veratrylidene-7-methoxychromanone (PERKIN, RÂY, and ROBINSON), 941.
Viscosity of aqueous solutions of strong electrolytes (SUGDEN), 174.

W.

Walden inversion (WARD), 1184.
Water vapour, adsorption of, on quartz and on platinum (LENHER), 1785.

X.

Xanthones, hydroxy-, preparation of (ATKINSON and HEILBRON), 2688.
Xanthorrhœa arborea, *hastilis*, and *reflexa*, volatile oils from (FINLAYSON), 2763.
p-**Xanthylphenylarsinic acid** (HEWITT, KING, and MURCH), 1369.
p-**Xylene**, equilibrium of sulphur and (HAMMICK and HOLT), 1995.
Xylidinodimethylbenzthiazoles, and their tetrabromides (HUNTER), 1403.
γ-**Xylose**, derivatives of (HAWORTH and WESTGARTH), 880.

Y.

Yeast, fixation of methylene blue by phosphoproteins of (RIWLIN), 2300.

Z.

Zinc, deposition of, on anodes in voltaic cells (HUMBY and PERRIN), 959.
diffusion of, in solid solution in copper (DUNN), 2973.
Zinc compounds, co-ordinated, optical activity of (MILLS and GOTTS), 3121.
Zinc sulphate, equilibrium of potassium sulphate, water, and (CAVEN and JOHNSTON), 2628.
Zinc organic compounds:—
Zincibenzoylpyruvic acid, brucine salt (MILLS and GOTTS), 3131.
Zinc anodes. See under Anodes.
Zirconium salts, reactions of, with sodium acetate, oxalate, and tartrate and with dextrose (BRITTON), 269.
Zirconium fluoride, analysis of (PRIDEAUX and ROPER), 898.

FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

CH_4 Methane, propagation of flame in mixtures of air and (CHAPMAN and WHEELER), 2139; extinction of flames of, by diluent gases (COWARD and HARTWELL), 1522.

CO Carbon monoxide, catalytic dissociation of (CLEMINSON and BRISCOE), 2148; ignition of mixtures of hydrogen and (CAMPBELL and WOODHEAD), 3010.

CS_2 Carbon disulphide, flame spectra of (EMELÉUS), 2948.

1 II

CHN Hydrocyanic acid, specific heat of (INGOLD), 26, 2816; (PARTINGTON), 1559; potassium salt, double salts of, with cadmium, mercury, nickel, and zinc cyanides (CORBET), 3190.

CH_2O_2 Formic acid, photochemical decomposition of aqueous solutions of (ALLMAND and REEVE), 2852; velocity of reaction of iodine with (HAMMICK and ZVEGINTZOV), 1105; sodium salt, reduction of silver acetate by (COUTIE), 887.

CH_4O Methyl alcohol, viscosity and density of (EWART and RAIKES), 1907; equilibrium between methyl formate and (CHRISTIANSEN), 413; influence of dissolved salts on miscibility temperatures of mixtures of paraffins with (HOWARD and PATTERSON), 2787.

CN_2H_5 Guanidine, hydrolysis of (BELL), 1213.

CSCl Thiocarbonyl chloride, interaction of, with chloro-substituted anilines (DYSON, GEORGE, and HUNTER), 3041.

1 III

CHNS Thiocyanic acid, ammonium salt, action of light on aqueous solutions of (HOLMES), 1690; (WERNER and BAILEY), 2970.

CH_5ON β-Methylhydroxylamine, determination of (BRADY and GOLDSTEIN), 2407.

C_2 Group.

C_2H_2 Acetylene, absorption of, by colloidal solutions (GATTERER), 299.

C_2H_4 Ethylene, reaction of bromine with (NORRISH and JONES), 55.

2 II

$C_2H_2O_4$ Oxalic acid, photochemical decomposition of aqueous solutions of (ALLMAND and REEVE), 2834; manganous salt, hydrates of (CHAMBERLAIN, HUME, and TOPLEY), 2620; sodium salt, reactions of, with salts of weak metallic bases (BRITTON), 269.

$C_2H_2Br_4$ Acetylene tetrabromide, action of, on organic bases (FULTON), 197.

C_2H_4O Acetaldehyde, photolysis of (BOWEN and WATTS), 1607.

$C_2H_4O_2$ Acetic acid, and its ammonium salt, equilibrium of water and (SUGDEN), 960; beryllium salt, conductivity of (SIDGWICK and LEWIS), 2539; magnesium salt, constitution of aqueous solutions of (RIVETT), 1063; silver salt, reduction of, by sodium formate (COUTIE), 887; sodium salt, reactions of, with salts of weak metallic bases (BRITTON), 269.

Methyl formate, equilibrium between methyl alcohol and (CHRISTIANSEN), 413.

C_2H_5I Ethyl iodide, preparation of (JONES and GREEN), 2760; reactions of, with sodium phenoxides in alcoholic solution (GOLDSWORTHY), 1254.

C_2H_6O Ethyl alcohol, temperature of maximum density of aqueous mixtures of (MCHUTCHISON), 1898; equilibria of, with alkali and alkaline earth salts (BONNELL and JONES), 318; influence of dissolved salts on miscibility temperatures of mixtures of paraffins with (HOWARD and PATTERSON), 2787; reactions of, with substituted carbamyl chlorides (PRICE), 3230.

2 III

C_2HOCl_3 Chloral, condensation of phenols with (CHATTAWAY), 2720.

$C_2H_3O_2Cl_3$ Chloral hydrate, effect of heat on (MOUNFIELD and WOOD), 498.

C_2H_5OBr Ethylene bromohydrin, preparation of (MCDOWALL), 499.

$C_2H_6O_4S$ Ethyl hydrogen sulphate (HAMID, SINGH, and DUNNICLIFF), 1098.

2 IV

$C_2H_2O_2ClBr$ Chlorobromoacetic acid, optical activity of, and its salts (READ and MCMATH), 2183.

$C_2H_3O_5ClS$ *dl*-Chlorosulphoacetic acid, resolution of, and its salts (READ and MCMATH), 2192.

$C_2H_{10}N_2Cl_2Cu_2$ Ethylenediammonium cuprochloride (MORGAN and BURSTALL), 2026.

$C_2H_{10}N_2Br_4Cu_2$ Ethylenediammonium cuprobromide (MORGAN and BURSTALL), 2026.

2 V

$C_2H_{16}O_{12}N_2Cl_2Cu$ Tetra-aquoethylenediamminocupric perchlorate (MORGAN and BURSTALL), 2026.

C_3 Group.

$C_3H_4O_4$ Malonic acid, beryllium salt, conductivity of (SIDGWICK and LEWIS), 2539.

C_3H_6O Acetone, photolysis of (BOWEN and WATTS), 1607; equilibrium of sodium iodide with (WADSWORTH and DAWSON), 2784; catalysis of the reaction of iodine with (DAWSON and CARTER), 2282; (DAWSON and DEAN), 2872.

3 III

$C_3H_{11}O_2N_3$ 3-Amino-2:4-diketotetrahydrothiazole, hydrochloride of (STEPHEN and WILSON), 2538.

$C_3H_7O_2N$ *dl*-Alanine, resolution of (KIPPING and POPE), 494.

3 IV

$C_3H_5O_2Cl_3Te$ Trichlorotelluripropionic acid (MORGAN and KELLETT), 1088.

$C_3H_5O_2Br_3Te$ Tribromotelluripropionic acid (MORGAN and KELLETT), 1088.

$C_3H_6ON_4S$ 3-Amino-2:4-diketotetrahydrothiazole-2-hydrazone, dihydrochloride of (STEPHEN and WILSON), 2538.

$C_3H_{14}N_3Cl_3I$ Triaminopropane dihydrochloride hydriodide (MANN and POPE), 2681.

3 V

$C_3H_{14}ON_3Cl_5Pt$ Tetrachloro(triaminopropanehydrochloride), platinum hydrate (MANN), 2687.

3 VI

$C_3H_{14}ON_3ClBr_4Pt$ Tetrabromo(triaminopropanehydrochloride), platinum hydrate (MANN), 2687.

C_4 Group.

$C_4H_6O_6$ Tartaric acid, oxidation of, by silver salts in solution (MAXTED), 2178; sodium salt, reactions of, with salts of weak organic bases (BRITTON), 269.

C_4H_8O Methyl ethyl ketone, equilibrium of, with sodium iodide (WADSWORTH and DAWSON), 2784.

$C_4H_8O_2$ Ethyl acetate, effect of salts and compounds on solubility of (GLASSTONE, DIMOND, and JONES), 2935; (GLASSTONE, DIMOND, and HARRIS), 2939.

$C_4H_{10}O$ Ethyl ether, flame spectra of (EMELÉUS), 2948.

4 III

$C_4H_5O_3N_3$ 4-Nitro-5-hydroxy-1-methylglyoxaline, and its salts (BALABAN), 571.

$C_4H_8O_2N_4$ Azodicarboxymethylamide (COOPER and INGOLD), 1895.

$C_4H_8O_2S$ Methyl β-thiolpropionate (DRUMMOND and GIBSON), 3076.

$C_4H_{10}O_2N_4$ Hydrazinedicarboxymethylamide (COOPER and INGOLD), 1895.

4 IV

$C_4H_7O_3N_4Cl$ Chlorobarbituric acid hydrazide (MACBETH, NUNAN, and TRAILL), 1251.

$C_4H_7O_3N_4Br$ Bromobarbituric acid hydrazide (MACBETH, NUNAN, and TRAILL), 1252.

4 V

$C_4H_7O_5NSAg_2$ Methyl silver β-thiolpropionate argentinitrate (DRUMMOND and GIBSON), 3076.

$C_4H_{10}ON_4I_2Cu$ Aquobisethylenediamminocupric iodide (MORGAN and BURSTALL), 2023.

$C_4H_{20}O_3N_4I_2Cu$ Diaquobisethylenediamminocupric iodide (MORGAN and BURSTALL), 2022.

C_5 Group.

C_5H_5N Pyridine, equilibrium of sulphur and (HAMMICK and HOLT), 1995; reaction between picric chloride and (HODGES), 2417; bromoaurate, and additive compound with acetylene tetrabromide (FULTON), 198.

$C_5H_7N_5$ 5-Diazo-3-propyl-1:2:4-triazoles, chloroaurates of (REILLY and DRUMM), 1735.

$C_5H_8O_2$ Acetylacetone, absorption spectra of (MORTON and ROSNEY), 706.

$C_5H_{10}O_5$ *d*-Arabinose, oxidation of (MCOWAN), 1747.

$C_5H_{10}N_4$ Aminopropyl-1:2:4-triazoles, and their salts (REILLY and DRUMM), 1729.

5 III

$C_5H_8O_2N_2$ Crotonylcarbamides (PHILLIPS), 2981.

$C_5H_8N_3Cl$ 5-Chloro-3-propyl-1:2:4-triazoles (REILLY and DRUMM), 1735.

$C_5H_9ON_5$ 3-Propyl-1:2:4-triazole-5-*iso*diazohydroxides (REILLY and DRUMM), 1735.

5 IV

$C_5H_6ON_2S$ 4:5-Dihydroiminazole-2-thioglycollo-1-lactam (STEPHEN and WILSON), 2535.

$C_5H_9O_2N_2Br$ α-Bromobutyrylcarbamide (PHILLIPS), 2981.

5 V

$C_5H_{20}ON_4I_2Cu$ Methanolbisethylenediamminocupric iodide (Morgan and Burstall), 2023.

C_6 Group.

C_6H_6 Benzene, vapour pressure of (Jolly and Vincent), 2156.

C_6H_{14} *n*-Hexane, effect of intensive drying on (Smits, de Liefde, Swart, and Claassen), 2666.

6 II

$C_6H_6O_2$ Pyrocatechol, crystal structure of (Caspari), 573.

Quinol, crystal structure of (Caspari), 2944.

$C_6H_6S_2$ *o*-Dithiolbenzene (Hurtley and Smiles), 1821.

C_6H_7O Mesityl oxide, absorption spectra of (Morton), 719.

C_6H_7N α-Picoline, additive compound with acetylene tetrabromide (Fulton), 199.

$C_6H_8N_2$ *dl-cis*-2:5-Dimethylpiperazine, preparation and resolution of (Kipping and Pope), 1076.

$C_6H_{10}O_3$ Ethyl acetoacetate, absorption spectra of (Morton and Rosney), 706.

$C_6H_{10}O_6$ δ-Gluconolactone, and δ-Mannonolactone, structure of (Haworth and Nicholson), 1901.

$C_6H_{12}O_3$ β-Methoxy*iso*valeric acid (Farmer and Kracovski), 2321.

$C_6H_{12}O_5$ γ-Methylxyloside (Haworth and Westgarth), 883.

Rhamnose, constitution of (Hirst and Macbeth), 22.

$C_6H_{12}O_6$ Dextrose, structure of (Charlton, Haworth, and Peat), 89; (Hirst), 350; action of, on zirconium chloride solutions (Britton), 269.

Fructose and γ-Fructose, structure of (Haworth and Hirst), 1858.

$C_6H_{18}N_4$ ββ′β″-Triaminotriethylamine, complex nickel and palladium salts (Mann and Pope), 482.

6 III

$C_6H_3N_6Fe$ Hydroferricyanic acid, salts, preparation and estimation of (Cumming and Good), 1924.

$C_6H_4O_5S_2$ Benzene-*o*-disulphonic anhydride (Hurtley and Smiles), 1824.

$C_6H_4N_6Fe$ Hydroferrocyanic acid, salts, preparation and estimation of (Cumming and Good), 1924; calcium, potassium, and sodium salts, solubilities of (Farrow), 49.

$C_6H_5O_2Cl$ 5-Chlororesorcinol (Hodgson and Wignall), 2827.

$C_6H_5O_2Br$ 5-Bromoresorcinol (Hodgson and Wignall), 2827.

$C_6H_5O_2I$ 5-Iodoresorcinol (Hodgson and Wignall), 2827.

$C_6H_6O_3S$ Benzenesulphonic acid, beryllium salt (Sidgwick and Lewis), 1290.

$C_6H_6N_2Cl$ *p*-Diazoiminobenzene hydrochloride (Gray), 3178.

$C_6H_{12}O_4N_2$ *i*-Dimethoxysuccinamide (Haworth and Hirst), 1865.

$C_6H_{13}O_2N$ *n*- and *iso*-Butyl glycines and their salts (Morgan), 80.

6 IV

$C_6H_2O_6N_3Cl$ Picryl chloride, reaction between pyridine and (Hodges), 2417.

$C_6H_2O_7N_3Br$ 3-Bromotrinitrophenols (Hodgson and Moore), 160.

$C_6H_3O_5N_2Br$ 3-Bromodinitrophenols (Hodgson and Moore), 158.

C_6H_4OBrAs *o*-Bromophenylarsenious oxide (Burton and Gibson), 457.

$C_6H_4O_3NCl$ Chloronitrobenzene, action of alcoholic potassium hydroxide on (Richardson), 522.

$C_6H_4O_3NCl$ 3-Chloro-2-nitrophenol (Hodgson and Moore), 158.

$C_6H_4O_3NBr$ 3-Bromonitrophenols (Hodgson and Moore), 157.

$C_6H_4O_3NI$ 3-Iodo-5-nitrophenol (Hodgson and Wignall), 2077.

$C_6H_5O_4NS_2$ Benzene-*o*-disulphonimide, and its silver salt (HURTLEY and SMILES), 1825.

$C_6H_5O_5NS_2$ Benzene-*o*-disulphonhydroxyimide ($+H_2O$) (HURTLEY and SMILES), 1824.

$C_6H_6N_2Cl_4Sb$ *p*-Diazoiminobenzene hydrochloride-antimony trichloride (GRAY), 3178.

$C_6H_7O_6N_2As$ 5-Nitro-4-amino-2-hydroxyphenylarsinic acid (HEWITT and KING), 825.

$C_6H_7O_6SAs$ *p*-Sulphophenylarsinic acid (HEWITT, KING, and MURCH), 1369.

$C_6H_9O_4N_2As$ 4:5-Diamino-2-hydroxyphenylarsinic acid (HEWITT and KING), 825.

$C_6H_{10}O_2N_2S$ Methyl 4:5-dihydroiminazole-2-thioglycollate (STEPHEN and WILSON), 2535.

$C_6H_{10}O_4S_2Ni$ Nickel thiopropionate (DRUMMOND and GIBSON), 3077.

$C_6H_{22}N_6I_2Ni$ Bistriaminopropanenickelous iodide (MANN and POPE), 2680.

$C_6H_{25}O_3N_6Co$ Bistriaminopropanecobaltic hydroxide, salts of (MANN and POPE), 2675.

6 V

$C_6H_2O_{10}NBrS$ 3-Bromo-2:5:6-trinitrophenol-4-sulphonic acid, potassium salt (HODGSON and MOORE), 161.

$C_6H_3O_4NIAs$ 5-Iodo-3-nitro-4-hydroxyphenylarsenious oxide (MACALLUM), 1647.

$C_6H_7O_4NIAs$ 5-Iodo-3-amino-4-hydroxyphenylarsinic acid, and its salts (MACALLUM), 1645.

$C_6H_{22}ON_4I_2Cu$ Ethanolbisethylenediamminocupric iodide (MORGAN, CARTER, and HARRISON), 2028.

$C_6H_{22}O_4N_6SNi$ Bistriaminopropanenickelous sulphate ($+5H_2O$) (MANN and POPE), 2680.

$C_6H_{26}ON_6Cl_{14}Pt_3$ Tetrachloro(triaminopropanehydrochloride)platinum chloroplatinate hydrate (MANN), 2687.

$C_6H_{28}O_2N_6Br_4Cu$ Bis(triaminopropanehydrobromide) cupric bromide dihydrate (MANN), 2686.

C_7 Group.

$C_7H_4S_3$ 2-Thio-1:3-benzdithiole (HURTLEY and SMILES), 1826.

$C_7H_6O_2$ Salicylaldehyde, condensation of, with benzyl methyl ketone (DICKINSON), 2234.

$C_7H_6O_3$ Salicylic acid, heat of combustion of (VERKADE and COOPS), 1437.

$C_7H_8O_4$ *cyclo*Pentene-1:2-dicarboxylic acids (HASSELL and INGOLD), 1469.

Piperylenedicarboxylic acid (HASSELL and INGOLD), 1468.

$C_7H_8N_2$ Benzamidine, nitrate of (FORSYTH, NIMKAR, and PYMAN), 802.

C_7H_9N Lutidine, additive compound with acetylene tetrabromide (FULTON), 198.

$C_7H_{10}O_4$ Acid, from methylation of ethyl *iso*propylidenemalonate (KON and SPEIGHT), 2730.

$C_7H_{10}O_5$ *cyclo*Pentanol-1:2-dicarboxylic acid, and its silver salt (HASSELL and INGOLD), 1468.

$C_7H_{11}N_3$ 2:3:4-Triaminotoluene (GORNALL and ROBINSON), 1983.

$C_7H_{14}O$ Methyl*cyclo*hexanols, isomerism of, and their esters (GOUGH, HUNTER, and KENYON), 2052.

$C_7H_{14}O_3$ Butyl lactates, rotatory dispersion of (WOOD, SUCH, and SCARF), 1928.

$C_7H_{14}O_6$ Methylfructose, transformation of, into derivatives of γ-fructose (ALLPRESS), 1720.

7 III

$C_7H_4OS_2$ 1:3-Benzdithiol-2-one (HURTLEY and SMILES), 1826.
$C_7H_4O_2Cl_2$ Dichloro-3-hydroxybenzaldehydes (HODGSON and BEARD), 152.
$C_7H_4O_2Br_4$ 2:4:5:6-Tetrabromo-3-hydroxyanisole (HODGSON and WIGNALL), 2826.
C_7H_5OF Fluorobenzaldehydes (SHOESMITH, SOSSON, and SLATER), 2760.
$C_7H_5O_2Cl$ Chloro-*m*-hydroxybenzaldehydes (HODGSON and BEARD), 149.
$C_7H_5O_2I$ 4-Iodo-2:5-toluquinone (HODGSON and MOORE), 2040.
$C_7H_5O_3N$ *m*-Nitrobenzaldehyde, condensation of quinaldine with (TAYLOR and WOODHOUSE), 2971.
$C_7H_5O_5N$ 5-Nitrosalicylic acid, crystallography of (CHATTAWAY and CURJEL), 3210.
$C_7H_5O_6N_3$ 2:3:4-Trinitrotoluene (GORNALL and ROBINSON), 1981.
$C_7H_5O_8N_3$ Trinitroguaiacols, and their salts (OXFORD), 2009.
$C_7H_5ClS_2$ 1:3-Benzdithiylium chloride (HURTLEY and SMILES), 2267.
$C_7H_6OI_2$ 3:5-Di-iodoanisole (HODGSON and WIGNALL), 2078.
$C_7H_6O_6N_2$ Dinitroguaiacols (OXFORD), 2008.
Dinitrohomocatechol (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1975.
$C_7H_6O_6S$ *m*-Carboxyphenylsulphuric acid, potassium salt (BURKHARDT and LAPWORTH), 689.
$C_7H_6N_2S$ ψ-Aminobenzthiazole, and its hydrochloride (HUNTER), 1397.
$C_7H_6N_2Se$ Selenocyanoaniline (CHALLENGER, PETERS, and HALÉVY), 1654.
C_7H_6ClBr Chlorobenzyl bromides (SHOESMITH and SLATER), 214.
C_7H_6BrI Bromobenzyl iodides (SHOESMITH and SLATER), 219.
C_7H_6BrF Fluorobenzyl bromides (SHOESMITH and SLATER), 220.
C_7H_7OCl Chloro-*m*-cresols (GIBSON), 1424.
4-Chlorocresols (HODGSON and MOORE), 2037.
C_7H_7OBr 4-Bromocresols (HODGSON and MOORE), 2037.
C_7H_7OI 4-Iodo-*o*-cresol (HODGSON and MOORE), 2037.
C_7H_7OF *o*-Fluoroanisole (HOLMES and INGOLD), 1329.
C_7H_7ONa Sodium benzyl oxide, reactions of, with alkyl iodides (GOLDSWORTHY), 1102.
$C_7H_7O_2N$ *o*-Nitrotoluene, mercuration of (COFFEY), 637; (BURTON, HAMMOND, and KENNER), 1802.
m- and *p*-Nitrotoluenes, mercuration of (COFFEY), 3215.
$C_7H_7O_2Cl$ 5-Chloro-3-hydroxyanisole (HODGSON and WIGNALL), 2826.
$C_7H_7O_2Br$ 5-Bromo-3-hydroxyanisole (HODGSON and WIGNALL), 2826.
$C_7H_7O_2I$ 5-Iodo-3-hydroxyanisole (HODGSON and WIGNALL), 2826.
$C_7H_7O_4N$ Nitroguaiacols (OXFORD), 2004.
$C_7H_8O_5N_2$ Nitro-*o*-anisidines (C. K. and E. H. INGOLD), 1318.
$C_7H_8O_3S$ *p*-Toluenesulphonic acid, beryllium salt (SIDGWICK and LEWIS), 1290.
$C_7H_8O_4Br_2$ 2:3-Dibromo*cyclo*pentane-1:2-dicarboxylic acid (HASSELL and INGOLD) 1469.
$C_7H_8O_5N_2$ 4-Nitro-2-aminotoluene-5-sulphonic acid, and its salts (COFFEY), 3221.
$C_7H_9O_2Br_3$ 3-Bromo-1:1-dimethyl-Δ^2-*cyclo*penten-2-ol-4-one (ROTHSTEIN and THORPE), 2017.
$C_7H_{11}O_2Cl$ Substance, from tellurium tetrachloride and keto-ethylenebisacetylacetone (MORGAN and TAYLOR), 48.
$C_7H_{11}O_4Na$ Diethyl sodiomalonate, action of, on ethyl citraconate or itaconate (INGOLD and SHOPPEE), 1912.
$C_7H_{11}O_6Tl_3$ Trithallium methylglucoside (FEAR and MENZIES), 939.
$C_7H_{12}ON_4$ 5-Acetylamino-3-*iso*propyl-1:2:4-triazole (REILLY and DRUMM), 1732.

$C_7H_{14}O_3N_2$ *n*-Butyl carbamidoacetate (MORGAN), 81.
ω-Ethoxymethylsuccinamide (INGOLD, SHOPPEE, and THORPE), 1487.
$C_7H_{15}O_3N$ *n*- and *iso*-Butyl alanines, and their salts (MORGAN), 82.

7 IV

$C_7H_2NCl_3S$ Trichlorophenylthiocarbimides (DYSON, GEORGE, and HUNTER), 3043.
$C_7H_3O_3NS_2$ Nitro-1:3-benzdithiol-2-one (HURTLEY and SMILES), 1826.
$C_7H_3O_4NCl_2$ Dichloronitro-3-hydroxybenzaldehydes, and their silver salts (HODGSON and BEARD), 2034.
$C_7H_3O_6N_2Cl$ Chlorodinitro-3-hydroxybenzaldehydes, and their salts (HODGSON and BEARD), 2035.
$C_7H_3NCl_2S$ 2:3-Dichlorophenylthiocarbimide (DYSON, GEORGE, and HUNTER), 3042.
$C_7H_4O_4NCl$ Chloronitro-3-hydroxybenzaldehydes, and their silver salts (HODGSON and BEARD), 2032.
$C_7H_4O_4N_2Cl_2$ 2:6-Dichloro-4-nitro-3-hydroxybenzaldoxime (HODGSON and BEARD), 2035.
$C_7H_4O_6N_2Cl$ 2-Chloro-4:6-dinitro-3-hydroxybenzaldoxime (HODGSON and BEARD), 2035.
$C_7H_4O_6N_2S$ 2:4-Dinitro-3-sulphobenzoic acid, sodium salt (GORNALL and ROBINSON), 1983.
C_7H_4NBrSe *p*-Bromophenyl selenocyanate (CHALLENGER, PETERS, and HALÉVY), 1655.
$C_7H_5ONS_2$ 2-Oximino-1:3-benzdithiole (HURTLEY and SMILES), 1826.
$C_7H_5O_2NCl_2$ Dichlorohydroxybenzaldoximes (HODGSON and BEARD), 152.
$C_7H_5O_4N_2Cl$ Chloronitro-3-hydroxybenzaldoximes (HODGSON and BEARD), 2032.
$C_7H_5O_3N_2F$ 4:6-Dinitro-2-fluoroanisole (HOLMES and INGOLD), 1330.
$C_7H_5N_2Cl_3S$ 3:4:6-Trichlorophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 3043.
$C_7H_5N_2Br_3S$ 5-Bromo-1-aminobenzthiazole dibromide (HUNTER), 1397.
$C_7H_5N_2SNa$ Sodium *o*-phenylenethiocarbamide (STEPHEN and WILSON), 2536.
$C_7H_6O_2NCl$ Chloro-*m*-hydroxybenzaldoximes (HODGSON and BEARD), 150.
4-Chloronitrosocresols (HODGSON and MOORE), 2037.
4-Chlorotoluquinone-5-oxime (HODGSON and MOORE), 2040.
$C_7H_6O_2NBr$ 4-Bromonitrosocresols (HODGSON and MOORE), 2038.
4-Bromotoluquinone-5-oxime (HODGSON and MOORE), 2040.
$C_7H_6O_2NI$ 4-Iodonitrosocresols (HODGSON and MOORE), 2038.
4-Iodotoluquinone-5-oxime (HODGSON and MOORE), 2040.
$C_7H_6O_2N_2Cl_2$ 2:6-Dichloro-4-nitro-*m*-toluidine (DAVIES and LEEPER), 1416.
$C_7H_6O_3NBr$ 3-Bromo-2-nitrophenyl methyl ether (HODGSON and MOORE), 158.
$C_7H_6O_3NI$ 3-Iodo-5-nitroanisole (HODGSON and WIGNALL), 2077.
$C_7H_6O_3NF$ Nitro-*o*-fluoroanisoles (HOLMES and INGOLD), 1330.
$C_7H_6O_6N_2S$ 3:5-Dinitro-2-hydroxyphenylmethylsulphone (POLLARD and ROBINSON), 3092.
$C_7H_6N_2Cl_2S$ 2:3-Dichlorophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 3042.
$C_7H_7ON_2Cl$ 2-Chloro-5-aminobenzaldoxime (HODGSON and BEARD), 151.
$C_7H_7OCl_3Te$ *p*-Anisyltelluritrichloride (MORGAN and KELLETT), 1084.
$C_7H_7O_3NS$ 5-Nitrothioguaiacol (HOLMES, C. K. and E. H. INGOLD), 1689.
$C_7H_7O_4NS$ 2-Nitrotoluenesulphinic acids (COFFEY), 642.
4-Nitrotoluenesulphinic acids, and their salts (COFFEY), 3220.

$C_7H_7O_5NS$ Nitroanisole-2-sulphinic acids (HOLMES, C. K. and E. H. INGOLD), 1688.

5-Nitro-2-hydroxyphenylmethylsulphone (POLLARD and ROBINSON), 3092.

3-Nitro-4-toluenesulphonic acid, salts of (HEWITT, KING, and MURCH), 1361.

4-Nitrotoluene-3-sulphonic acid, and its salts (COFFEY), 3222.

C_7H_8ONCl 3-Chloro-5-aminoanisole (HODGSON and WIGNALL), 2078.

4-Chloro-5-amino-*o*-cresol (HODGSON and MOORE), 2038.

Chloroanisidines, and their hydrochlorides (HODGSON and HANDLEY), 543.

C_7H_8ONBr 3-Bromo-5-aminoanisole (HODGSON and WIGNALL), 2078.

C_7H_8ONI 3-Iodo-5-aminoanisole (HODGSON and WIGNALL), 2078.

4-Iodoaminocresols (HODGSON and MOORE), 2038.

$C_7H_8N_2ClS$ ψ-Aminotoluthiazoles, and their hydrochlorides (HUNTER), 1397.

$C_7H_{10}O_3N_2S$ *m*-Tolylenediamine-3-sulphonic acid, sodium salt (GORNALL and ROBINSON), 1982.

$C_7H_{12}O_2N_2S$ Ethyl 4:5-dihydroiminazole-2-thioglycollate (STEPHEN and WILSON), 2535.

7 V

$C_7H_6O_2NClHg$ Chloromercurinitrotoluenes (COFFEY), 638, 3218.

C_8 Group.

C_8H_{10} *p*-Xylene, equilibrium of sulphur and (HAMMICK and HOLT), 1995.

8 II

$C_8H_6O_3$ *o*-Piperonal (PERKIN and TRIKOJUS), 2931.

$C_8H_6O_4$ *o*-Piperonylic acid (PERKIN and TRIKOJUS), 2929.

$C_8H_8N_2$ Phenylenediacetonitriles, reduction of (TITLEY), 508.

$C_8H_{10}O_2$ *iso*Creosol (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1972.

$C_8H_{10}O_4$ *cyclo*Pentylidenemalonic acid (KON and SPEIGHT), 2731.

$C_8H_{12}O_3$ Ethyl *cyclo*pentanone-3-carboxylate (INGOLD, SHOPPEE, and THORPE), 1486.

$C_8H_{12}O_4$ Dihydrosuberocolic acid (GOSS and INGOLD), 1474.

$C_8H_{14}O_5$ Trimethyl γ-arabonolactone, structure of (HAWORTH and NICHOLSON), 1900.

Trimethyl xylonolactones (HAWORTH and WESTGARTH), 885.

$C_8H_{14}O_6$ αα′-Dihydroxysuberic acid (GOSS and INGOLD), 1473.

$C_8H_{14}S_6$ Ethylene trithioformate (HURTLEY and SMILES), 2268.

$C_8H_{16}O$ Methyl*cyclo*hexylcarbinol, resolution of (DOMLEO and KENYON), 1841.

$C_8H_{16}O_5$ Trimethyl γ-xylose (HAWORTH and WESTGARTH), 885.

$C_8H_{16}O_6$ Dimethyl glucose, new crystalline form of (HAWORTH and SEDGWICK), 2579.

Methyl methylfructoside (ALLPRESS), 1722.

8 III

$C_8H_4O_2S_2$ 1:4-Benzdithian-2:3-dione (HURTLEY and SMILES), 2268.

$C_8H_5O_2Cl_3$ 2:4:6-Trichloro-3-methoxybenzaldehyde (HODGSON and BEARD), 155.

$C_8H_5O_3N$ 2:3-Methylenedioxybenzonitrile (PERKIN and TRIKOJUS), 2930.

$C_8H_5O_3Cl$ 2:3-Methylenedioxybenzoyl chloride (PERKIN and TRIKOJUS), 2929.

$C_8H_6O_3Cl$ Dichloro-3-methoxybenzaldehydes (HODGSON and BEARD), 154.

$C_8H_6O_2Cl_2$ 3:5-Dichlorophenyl acetate (HODGSON and WIGNALL), 2078.

$C_8H_6O_2Br_2$ 3:5-Dibromophenyl acetate (HODGSON and WIGNALL), 2078.

$C_8H_6O_3Cl_2$ 2:6-Dichloro-3-methoxybenzoic acid (HODGSON and BEARD), 155.

C_8H_6NBr 6-Bromo-*o*-toluonitrile (BURTON, HAMMOND, and KENNER), 1803.

$C_8H_7ON_3$ Acetyl-1:2:3-benztriazole (BELL and KENYON), 954.

$C_8H_7O_2N$ *o*-Piperonaloximes (PERKIN and TRIKOJUS), 2931.
$C_8H_7O_2Cl$ Chloro-3-methoxybenzaldehydes (HODGSON and BEARD), 154.
Phenylchloroacetic acid, action of water on (WARD), 1184.
$C_8H_7O_2Br$ Phenylbromoacetic acid, action of water on (WARD), 1184.
$C_8H_7O_3N$ 2-β-Methylenedioxybenzamide (PERKIN and TRIKOJUS), 2930.
$C_8H_7O_3Cl$ Chloro-*m*-methoxybenzoic acids (GIBSON), 1428.
$C_8H_7O_5N_3$ *N*-Methyl-2:4-dinitrobenzaldoxime (BRADY, DUNN, and GOLDSTEIN), 2393.
$C_8H_7O_6N_3$ 3:5-Dinitro-*N*-acetyl-*o*-aminophenol (C. K. and E. H. INGOLD), 1321.
C_8H_7NSe *p*-Tolyl selenocyanate (CHALLENGER, PETERS, and HALÉVY), 1654.
$C_8H_8OCl_2$ 2:5-Dichloro-*m*-tolyl methyl ether (GIBSON), 1426.
$C_8H_8O_3N_2$ 2:3-Methylenedioxybenzenylamino-oxime (PERKIN and TRIKOJUS), 2930.
o-Nitrobenzomethylamide (BRADY and DUNN), 2415.
$C_8H_8O_3S$ *dl-m*-Carboxyphenyl methyl sulphoxide, resolution of, and its salts (HARRISON, KENYON, and PHILLIPS), 2088.
$C_8H_8O_4N_2$ Nitroacetylaminophenols (HEWITT and KING), 822; (C. K. and E. H. INGOLD), 1322.
$C_8H_8O_5N_2$ 2:4-Dinitro-3-methoxytoluene (GORNALL and ROBINSON), 1984.
$C_8H_8O_6N_2$ 2:6-Dinitrocreosols, and their salts (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1973.
$C_8H_8O_8N_2$ 3:6-Dinitroveratrole (OXFORD), 2008.
$C_8H_8N_2S$ 1-Aminomethylbenzthiazoles (HUNTER), 1398.
1-Imino-2-methyl-1:2-dihydrobenzthiazole (HUNTER), 1393.
1-Methylaminobenzthiazole (HUNTER), 1394.
C_8H_9OCl Chloro-*m*-tolyl methyl ethers (GIBSON), 1425.
$C_8H_9O_4N$ 2-Nitro-3-hydroxy-*p*-tolyl methyl ether (GULLAND and ROBINSON), 1980.
$C_8H_{10}OS$ *S*-Methylthioguaiacol, nitration of (POLLARD and ROBINSON), 3090; (C. K. and E. H. INGOLD), 3093.
$C_8H_{10}O_2S$ 2-Methoxyphenyl methyl sulphoxide (POLLARD and ROBINSON), 3091.
$C_8H_{10}O_2N$ Nitro-*N*-methyl-*o*-anisidines (C. K. and E. H. INGOLD), 1325.
$C_8H_{10}O_4N_2$ 2-Nitro-6-amino*iso*creosol (GULLAND and ROBINSON), 1979.
$C_8H_{10}O_4S_2$ Benzene-*o*-dimethylsulphone (HURTLEY and SMILES), 1825.
$C_8H_{11}ON$ *p*-Phenetidine, zincichloride of (BANFIELD and KENYON), 1625.
$C_8H_{12}O_2N_2$ 3:6-Diaminoveratrole (OXFORD), 2008.
Dimethoxyphenylhydrazines, and their hydrochlorides (PERKIN and RUBENSTEIN), 357.
$C_8H_{12}O_4Br_2$ αα′-Dibromosuberic acid (GOSS and INGOLD), 1473.
$C_8H_{14}O_4N_4$ Butane-ααβγ-tetracarboxyamide (INGOLD and SHOPPEE), 1917.

8 IV

$C_8H_6O_4NCl$ Chloronitro-3-methoxybenzaldehydes (HODGSON and BEARD), 2032.
3-Chloro-5-nitrophenyl acetate (HODGSON and WIGNALL), 2077.
$C_8H_6O_4NBr$ 3-Bromo-5-nitrophenyl acetate (HODGSON and WIGNALL), 2077.
$C_8H_6O_4NI$ 3-Iodo-5-nitrophenyl acetate (HODGSON and WIGNALL), 2077.
$C_8H_6O_4N_4Cl_2$ Dichloronitro-3-hydroxybenzaldehyde semicarbazones (HODGSON and BEARD), 2035.
$C_8H_6O_6N_3Cl$ Chlorodinitro-3-hydroxybenzaldehyde semicarbazones (HODGSON and BEARD), 2035.
C_8H_7ONS 2-Keto-1-methyl-1:2-dihydrobenz*iso*thiazole (MCCLELLAND and GAIT), 923.

$C_8H_7O_4N_4Cl$ Chloronitro-3-hydroxybenzaldehyde semicarbazones (HODGSON and BEARD), 2032.

$C_8H_7N_2BrS$ Bromo-1-amino-3-methylbenzthiazole, and its hydrobromide (HUNTER), 1398.

5-Bromo-1-methylaminobenzthiazole (HUNTER and SOYKA), 2962.

$C_8H_7N_2Br_7S$ 5-Bromo-1-methylaminobenzthiazole hexabromide (HUNTER and SOYKA), 2961.

C_8H_8ONCl 6-Chloro-2-nitro-*m*-tolyl methyl ether (GIBSON), 1427.

Methyl-*p*-chlorobenzaldoximes (BRADY, DUNN, and GOLDSTEIN), 2391.

$C_8H_8ON_2Cl$ *p*-Acetylaminobenzenediazonium chloride (GRAY), 3178.

$C_8H_8OBr_2S$ 3:5-Dibromo-*S*-methylthioguaiacol (HOLMES, C. K. and E. H. INGOLD), 1690.

$C_8H_8O_2NCl$ Chloro-3-methoxybenzaldoximes (HODGSON and BEARD), 154.

$C_8H_8O_2N_2Cl$ Chloro-*m*-hydroxybenzaldehyde semicarbazones (HODGSON and BEARD), 150.

$C_8H_8N_2Br_2S$ 1-Imino-2-methyl-1:2-dihydrobenzthiazole dibromide (HUNTER), 1392.

Methylaminobenzthiazole dibromides (HUNTER), 1393, 1398, 2954.

$C_8H_8N_2Br_4S$ Methylaminobenzthiazole tetrabromides (HUNTER), 1393, 1399.

$C_8H_9OCl_3Te$ Methoxytolyltelluritrichlorides (MORGAN and KELLETT), 1086.

$C_8H_9O_2N_2I$ 4-Iodo-2-nitrodimethylaniline (AITKEN and READE), 1897.

$C_8H_9O_3NS$ Acetanilide-*m*-sulphinic acid (CHILD and SMILES), 2699.

2- and 4-Nitro-5-methoxythioanisoles (HODGSON and HANDLEY), 544.

Nitromethylthioguaiacols (HOLMES, C. K. and E. H. INGOLD), 1687.

$C_8H_9O_3N_2Cl$ *N*-Methylnitrobenzaldoxime hydrochlorides (BRADY, DUNN, and GOLDSTEIN), 2394.

$C_8H_9O_4NS$ 4-Nitro-2-methoxyphenylmethylsulphoxide (HOLMES, C. K. and E. H. INGOLD), 1689.

5-Nitro-2-methoxyphenyl methyl sulphoxide (POLLARD and ROBINSON), 3091; (C. K. and E. H. INGOLD), 3093.

$C_8H_9O_5NS$ Nitro-2-methoxyphenylmethylsulphones (HOLMES, C. K. and E. H. INGOLD), 1687.

$C_8H_9O_5N_2Cr$ Acetylaminobenzenediazonium chromates (GRAY), 3180.

$C_8H_9N_2BrS$ *s*-*p*-Bromophenylmethylthiocarbamide (HUNTER and SOYKA), 2961.

$C_8H_{10}ONCl$ Chloro-3-methoxy-*o*-toluidines (GIBSON), 1426.

N-Methylbenzaldoxime hydrochloride (BRADY, DUNN, and GOLDSTEIN), 2394.

$C_8H_{10}O_3N_2S$ Dimethoxydiazobenzenesulphonic acids, ammonium salts (PERKIN and RUBENSTEIN), 359.

$C_8H_{11}ONS$ Anisidinemethyl thioethers, and their hydrochlorides (HODGSON and HANDLEY), 545.

$C_8H_{11}O_4NS_2$ *o*-Ethylsulphonylbenzenesulphonamide (HURTLEY and SMILES), 1824.

$C_8H_{12}O_6N_2S$ Dimethoxyphenylhydrazinosulphonic acids, ammonium salts (PERKIN and RUBENSTEIN), 359.

$C_8H_{13}ON_4Cl$ δ-Methylanilinosemicarbazide hydrochloride (BAIRD and WILSON), 2373.

$C_8H_{14}O_4S_2Ni$ Ethyl nickel thiolacetate (DRUMMOND and GIBSON), 3076.

Methyl nickel β-thiolpropionate (DRUMMOND and GIBSON), 3076.

$C_8H_{16}ON_8Cu_3$ Aquobisethylenediamminocupric cuprocyanide (MORGAN and BURSTALL), 2023.

$C_8H_{32}O_8N_6Cu$ Bismethanolbisethylenediamminocupric cyanate tetrahydrate (MORGAN and BURSTALL), 2027.

8 V

$C_8H_7O_3NIAs$ 5-Iodo-3-acetylamino-4-hydroxyphenylarsenious oxide ($+1\frac{1}{2}H_2O$) (MACALLUM), 1647.

$C_8H_8O_2NIS$ Acetanilide-*p*-sulphonyl iodide (CHILD and SMILES), 2701.

$C_8H_9O_5NIAs$ 5-Iodo-3-acetylamino-4-hydroxyphenylarsinic acid (MACALLUM), 1646.

C_9 Group.

C_9H_{10} Methylstyrenes (TITLEY), 517.

9 II

$C_9H_4O_4$ 3:4-Methylenedioxyphthalide (PERKIN and TRIKOJUS), 2930.

$C_9H_6O_6$ Normeconinecarboxylic acid (PERKIN and TRIKOJUS), 2927.

C_9H_7N Quinoline, equilibrium of sulphur and (HAMMICK and HOLT), 1995.

Quinolines, bromoaurates, and additive compounds with acetylene tetrabromide (FULTON), 198.

$C_9H_{10}O$ Benzyl methyl ketone, condensation of, with salicylaldehyde (DICKINSON), 2234.

$C_9H_{10}O_3$ *p*-Hydroxy-ω-methoxyacetophenone (ROBERTSON and ROBINSON), 1715.

$C_9H_{12}O_4$ Methyl hydrogen Δ^3-tetrahydro*iso*phthalate (FARMER and RICHARDSON), 2175.

Acid, from methylation of ethyl *cyclo*pentylidene malonate (KON and SPEIGHT), 2732.

$C_9H_{13}N$ β-Tolylethylamines, and their salts (TITLEY), 517.

$C_9H_{14}O_4$ *cis-o*-Carboxy*cyclo*hexaneacetic acid, preparation of (KON and QUDRAT-I-KHUDA), 3071.

Ethyl citraconate or itaconate, action of ethyl sodiomalonate on (INGOLD and SHOPPEE), 1912.

1-Methyl 1′-hydrogen *cyclo*hexane-1:1′-carboxylate (WIGHTMAN), 2543.

$C_9H_{14}O_5$ α-Ketoazelaic acid (GOSS and INGOLD), 1477.

$C_9H_{16}O_6$ αα′-Dihydroxyazelaic acid, and its silver salt (GOSS and INGOLD), 1476.

αα′-Dimethoxypimelic acids, and their silver salts (HASSELL and INGOLD), 1470.

$C_9H_{18}O_6$ Trimethylglucose, new crystalline form of (HAWORTH and SEDGWICK), 2573.

$C_9H_{14}O$ *iso*Phorone, reactions of (BAKER), 663.

$C_9H_{24}N_4$ Triaminotripropylamine, salts of (MANN and POPE), 491.

9 III

$C_9H_6O_2Br_2$ 6:ω-Dibromo-3:4-methylenedioxystyrene (HAWORTH, PERKIN, and STEVENS), 1766.

$C_9H_6N_2Br_2$ 4:5-Dibromo-2-phenylglyoxaline, and its salts (FORSYTH, NIMKAR, and PYMAN), 806.

$C_9H_7O_3Cl$ 2-Chloro-3-acetoxybenzaldehyde (HODGSON and BEARD), 150.

$C_9H_7O_7N_3$ Allyl 2:4:6-trinitrophenyl ether (FAIRBOURNE and FOSTER), 3148.

$C_9H_7N_2Br$ 4(5)-Bromo-2-phenylglyoxaline, and its salts (FORSYTH, NIMKAR, and PYMAN), 807.

$C_9H_9O_5N_3$ Methyl-6-nitro-3:4-methylenedioxybenzaldoximes (BRADY, DUNN, and GOLDSTEIN), 2391.

$C_9H_9O_3N_3$ 2-*m*-Nitrophenyl-4:5-dihydroglyoxaline, salts of (FORSYTH, NIMKAR, and PYMAN), 805.

$C_9H_9O_3N$ 3:4-Methylenedioxybenzomethylamide (BRADY and DUNN), 2415.

Methyl-3:4-methylenedioxybenzaldoximes (BRADY, DUNN, and GOLDSTEIN), 2389.

$C_9H_9O_5N$ Ethyl 5-nitrosalicylate, crystallography of (CHATTAWAY and CURJEL), 3214.

5-Nitro-2-ethoxybenzoic acid (CHATTAWAY), 2724.

$C_9H_{10}O_4N_2$ *β-O*-Methyl-3-nitro-*p*-methoxybenzaldoxime (BRADY, DUNN, and GOLDSTEIN), 2402.

Nitroaceto-*o*-anisidides (C. K. and E. H. INGOLD), 1317, 1319.

$C_9H_{10}O_6N_2$ 4:5-Dinitro-2-ethoxyanisole (ALLAN and ROBINSON), 378.

2:6-Dinitrohomoveratrole (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1976.

$C_9H_{10}N_2S$ 1-Amino-3:5-dimethylbenzthiazole (HUNTER), 1400.

1-Ethylaminobenzthiazole (HUNTER), 2955.

1-Imino-2-ethyl-1:2-dihydrobenzthiazole (HUNTER), 1394.

$C_9H_{10}N_2Se$ Selenocyanodimethylaniline (CHALLENGER, PETERS, and HALÉVY), 1654.

$C_9H_{10}ClAs$ *As*-Chlorotetrahydroarsinoline (ROBERTS, TURNER, and BURY), 1445.

$C_9H_{11}O_2N$ *p*-Methoxybenzomethylamide (BRADY and DUNN), 2416.

Methylmethoxybenzaldoximes (BRADY, DUNN, and GOLDSTEIN), 2391.

$C_9H_{11}O_3N$ Phenylserines, isomeric (FORSTER and RAO), 1943.

$C_9H_{11}O_3Br$ 5-Bromo-2:3-dimethoxybenzyl alcohol (RUBENSTEIN), 650.

$C_9H_{11}O_4N$ Nitro-4-ethoxyanisoles (ROBINSON and SMITH), 395.

$C_9H_{11}O_5N$ 5-Nitro-2:3-dimethoxybenzyl alcohol (RUBENSTEIN), 649.

$C_9H_{12}OBr_4$ Tetrabromo-3:3:5-trimethyl*cyclo*hexan-1-one (BAKER), 668.

$C_9H_{12}O_2N_2$ *m*-Nitrobenzyldimethylamine (GOSS, INGOLD, and WILSON), 2458.

cis-Phenylserine amide (FORSTER and RAO), 1948.

$C_9H_{12}O_2N_2$ 4-Nitro-*NN*-dimethyl-*o*-anisidine (C. K. and E. H. INGOLD), 1326.

$C_9H_{12}O_4N$ 5-Amino-2:3-dimethoxybenzoic acid (RUBENSTEIN), 652.

2-Nitro-6-aminohomoveratrole, and its hydrochloride (GULLAND and ROBINSON), 1979.

$C_9H_{15}O_2N$ 1-Methyl 1′-carbamyl*cyclo*hexane-1-carboxylate (WIGHTMAN), 2544.

$C_9H_{15}O_3N_3$ Ethyl *cyclo*pentanone-3-carboxylate semicarbazone (INGOLD, SHOPPEE, and THORPE), 1486.

$C_9H_{15}OBr$ Bromo*iso*phorone (BAKER), 668.

$C_9H_{16}O_4N_2$ *αα′*-Dimethoxypimelamides (HASSELL and INGOLD), 1470.

$C_9H_{19}O_2N$ *n*-Butyl valine, and its salts (MORGAN), 83.

9 IV

$C_9H_5O_2N_3Br_2$ 4:5-Dibromo-2-nitrophenylglyoxalines (FORSYTH, NIMKAR, and PYMAN), 806.

$C_9H_6ON_2S$ Benziminazole-2-thioglycollo-1-lactam (STEPHEN and WILSON), 2536.

$C_9H_6O_2N_3Br$ 4(5)-Bromo-2-*p*-nitrophenylglyoxaline (FORSYTH, NIMKAR, and PYMAN), 807.

$C_9H_7O_3N_2Cl_3$ 2:6-Dichloro-4-nitrochloroaceto-*m*-toluidide (DAVIES and LEEPER), 1417.

$C_9H_7O_5NS$ Phthalimidomethanesulphonic acid, and its barium salt (BALABAN), 573.

$C_9H_7O_7N_3Br_2$ Dibromo-derivative of allyl 2:4:6-trinitrophenyl ether (FAIRBOURNE and FOSTER), 3148.

$C_9H_8ON_2S$ 1-Imino-2-acetyl-1:2-dihydrobenzthiazole (HUNTER), 1395.

$C_9H_8O_2NBr$ 3-Bromo-2-acetylaminobenzoic acid (BURTON, HAMMOND, and KENNER), 1803.

$C_9H_8O_4NBr$ Ethyl 3-bromonitrobenzoate (BURTON, HAMMOND, and KENNER), 1804.

$C_9H_9O_5N_2Cl$ *N*-Methyl-6-nitro-3:4-methylenedioxybenzaldoxime hydrochloride (BRADY, DUNN, and GOLDSTEIN), 2394.

$C_9H_9N_2BrS$ 5-Bromo-1-ethylaminobenzthiazole (HUNTER and SOYKA), 2962.
$C_9H_9N_2Br_3S$ 5-Bromo-1-ethylaminobenzthiazole dibromide and 5-Bromo-1-ethylimino-1:2-dihydrobenzthiazole dibromide (HUNTER and SOYKA), 2962.
$C_9H_{10}ONBr$ Acetyl-3-bromo-*o*-toluidine (BURTON, HAMMOND, and KENNER), 1803.
$C_9H_{10}ONI$ 1-Methylbenzoxazole methiodide (CLARK), 234.
$C_9H_{10}O_3NCl$ *N*-Methyl-3:4-methylenedioxybenzaldoxime hydrochloride (BRADY, DUNN, and GOLDSTEIN), 2394.
$C_9H_{10}O_4NBr$ 6-Bromo-2-nitrohomoveratrole (GULLAND and ROBINSON), 1979.
$C_9H_{10}O_5NCl$ 1-Methylbenzoxazole methoperchlorate (CLARK), 234.
$C_9H_{10}N_2Br_2S$ 1-Ethylaminobenzthiazole dibromide (HUNTER), 2955.
$C_9H_{10}N_2Br_4S$ 1-Amino-3-5-dimethylbenzthiazole tetrabromide (HUNTER), 1399.
1-Imino-2-ethyl-1:2-dihydrobenzthiazole tetrabromide (HUNTER), 1394.
$C_9H_{11}ONS$ 2-Acetylaminotolyl 5-mercaptan (CHILD and SMILES), 2700.
$C_9H_{11}O_3NS$ *p*-Acetylaminophenylmethylsulphone (CHILD and SMILES), 2699.
2-Acetylaminotoluene-5-sulphinic acid (CHILD and SMILES), 2700.
$C_9H_{11}O_4S_2As$ *p*-Xanthylphenylarsinic acid (HEWITT, KING, and MURCH), 1369.
$C_9H_{11}N_2BrS$ *s*-*p*-Bromophenylethylthiocarbamide (HUNTER and SOYKA), 2962.
$C_9H_{12}O_2NCl$ *N*-Methylmethoxybenzaldoxime hydrochlorides (BRADY, DUNN, and GOLDSTEIN), 2394.
$C_9H_{12}O_2NI$ *N*-Methylmethoxybenzaldoxime hydriodides (BRADY, DUNN, and GOLDSTEIN), 2396.
$C_9H_{12}O_7N_2S$ *N*-Methylnitrobenzaldoxime methosulphates (BRADY, DUNN, and GOLDSTEIN), 2394.
$C_9H_{13}O_5NS$ *N*-Methylbenzaldoxime methosulphate (BRADY, DUNN, and GOLDSTEIN), 2395.
$C_9H_{13}NClBr$ *p*-Bromophenyltrimethylammonium chloride (READE), 2531.

9 V

$C_9H_7ON_2BrS$ 5-Bromo-1-acetylaminobenzthiazole (HUNTER), 1398.
5-Bromo-1-imino-2-acetyl-1:2-dihydrobenzthiazole (HUNTER), 1398.
$C_9H_8ON_2Br_2S$ 1-Imino-2-acetyl-1:2-dihydrobenzthiazole dibromide (HUNTER), 1394.
$C_9H_8ON_2Br_4S$ 1-Acetylaminobenzthiazole tetrabromide (HUNTER), 1395.
$C_9H_8ON_2Br_6S$ 1-Acetylaminobenzthiazole hexabromide (HUNTER), 1397.
$C_9H_{10}ON_2Br_2S$ 1-Imino-2-acetyl-1:2-dihydrobenzthiazole dibromide hydrobromide (HUNTER), 1395.
$C_9H_{10}O_3NClS$ 2-Acetylaminotoluene-5-sulphonyl chloride (CHILD and SMILES), 2700.
$C_9H_{10}O_6NCl$ 5-Nitrohomoveratrole-6-sulphonyl chloride (GULLAND and ROBINSON), 1977.
$C_9H_{11}O_6NIAs$ 5-Iodo-3-carbethoxyamino-4-hydroxyphenylarsinic acid (MACALLUM), 1646.

C_{10} Group.

$C_{10}H_{12}$ α-Ethylstyrene (JOHNSON and KON), 2755.
$C_{10}H_{14}$ *d*-*sec*.-Butylbenzene, preparation and rotation of (HARRISON, KENYON, and SHEPHERD), 658.

10 II

$C_{10}H_8O_5$ 3:4-Methylenedioxyhomophthalic anhydride (HAWORTH, PERKIN, and STEVENS), 1769.
$C_{10}H_8O_4$ 2:3-Methylenedioxycinnamic acid (PERKIN and TRIKOJUS), 2932.

$C_{10}H_8O_5$ 3-Hydroxy-4-methoxyphthalidecarboxylic acid (PERKIN and TRIKOJUS), 2928.

3:4-Methylenedioxyhomophthalic acid (HAWORTH, PERKIN, and STEVENS), 1769.

Methyl normeconinecarboxylate (PERKIN and TRIKOJUS), 2928.

$C_{10}H_9N$ Quinaldine, condensation of, with *m*-nitrobenzaldehyde (TAYLOR and WOODHOUSE), 2971.

$C_{10}H_{10}O_2$ β-Phenyl-Δ$^{\beta}$-butenoic acid (JOHNSON and KON), 2752.

Styrylacetic acid, and its potassium salt (LINSTEAD and WILLIAMS), 2741.

$C_{10}H_{10}O_4$ ω-Acetoxy-4-hydroxyacetophenone (NOLAN, PRATT, and ROBINSON), 1969.

Ethyl *o*-piperonylate (PERKIN and TRIKOJUS), 2929.

$C_{10}H_{11}N$ 1:2-Dihydroquinaldine, synthesis of (MASON), 955.

$C_{10}H_{12}O_3$ Acetyl*iso*creosol (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1973.

*p-iso*Propoxybenzoic acid (BRADLEY and ROBINSON), 2361.

$C_{10}H_{12}O_4$ Ethyl *p*-methoxyphenyl carbonate (ROBINSON and SMITH), 394.

$C_{10}H_{12}O_{10}$ Dicarbomethoxyarabinose carbonate (HAWORTH and MAW), 1752.

$C_{10}H_{13}N$ 1-Methyl-Δ$^{1:3}$-*cyclo*hexadienyl-3-propionitrile (FARMER and ROSS), 1576.

$C_{10}H_{14}O_2$ 1:3-Diketodecahydronaphthalene (KON and QUDRAT-I-KHUDA), 3071.

*cyclo*Hexane*spirocyclo*pentane-2:4-dione (ROTHSTEIN and THORPE), 2016.

$C_{10}H_{14}O_4$ Ethyl hydrogen Δ^{2}-tetrahydro*iso*phthalate (FARMER and RICHARDSON), 2174.

Ethyl mesityloxido-oxalate, absorption spectra of (MORTON and ROGERS), 713.

Methyl tetrahydro*iso*phthalates (FARMER and RICHARDSON), 2176.

Acid, from methylation of ethyl Δ^{1}-*cyclo*hexenylmalonate (KON and SPEIGHT), 2734.

$C_{10}H_{14}O_8$ βδ-Dicarboxysuberic acid (INGOLD and SHOPPEE), 1917.

$C_{10}H_{14}N_2$ Benzenyltrimethylamidine, nitrate of (FORSYTH, NIMKAR, and PYMAN), 803.

Nicotine, bromoaurate and additive compound with acetylene tetrabromide (FULTON), 198.

$C_{10}H_{15}N$ β-Tolylethylmethylamines, and their salts (TITLEY), 517.

$C_{10}H_{16}O$ Carone, catalytic hydrogenation of (IYER and SIMONSEN), 2049.

Piperitone, condensation of, with aldehydes (EARL and READ), 2072.

Sabinol, oxidation of, with hydrogen peroxide (HENDERSON and ROBERTSON), 2761.

$C_{10}H_{16}O_3$ 1-Acetyl*cyclo*hexane-1-acetic acid (ROTHSTEIN and THORPE), 2016.

Acid, from hydrolysis of substance $C_{12}H_{19}O_3N$ (KON and NUTLAND), 3108.

$C_{10}H_{16}O_4$ Dimethyl *cyclo*hexane-1:1-dicarboxylate (WIGHTMAN), 2543.

$C_{10}H_{16}N$ Benzyltrimethylamine, nitrate of (ING and ROBINSON), 1666.

$C_{10}H_{16}N_8$ 3:3′-Di-*n*-propyl-5:5′-azo-1:2:4-triazole (REILLY and DRUMM), 1733.

$C_{10}H_{18}O_4$ Tetramethyladipic acids, electrolytic synthesis of (FARMER and KRACOVSKI), 2318.

$C_{10}H_{18}O_6$ αα′-Dimethoxysuberic acid (GOSS and INGOLD), 1475.

$C_{10}H_{20}O$ γη-Dimethyloctan-ε-one (JONES), 2769.

$C_{10}H_{20}O_6$ Tetramethyl γ-fructose, oxidation of (MCOWAN), 1743.

Tetramethylglucose, mutarotation of (JONES and LOWRY), 720; (FAULKNER and LOWRY), 1940; oxidation of (HIRST), 351.

$C_{10}H_{21}N$ *dl*-Menthylamines, salts of (READ, COOK, and SHANNON), 2226.

10 III

$C_{10}H_6O_2Cl_6$ Anhydro-2-ββδ-trichloro-α-hydroxyethoxy-1-ββδ-trichloro-α-hydroxyethylbenzene (CHATTAWAY), 2726.

$C_{10}H_6O_3N_2$ 8-Nitroquinoline-2-aldehyde (HAMMICK), 1301.
$C_{10}H_7ON$ Quinoline-2-aldehyde (HAMMICK), 1303.
$C_{10}H_7O_2N$ *o*-Cyano*allo*cinnamic acid, preparation of (EDWARDS), 815.
$C_{10}H_7O_2Br$ 4-Bromo-6:7-methylenedioxy-1-hydrindone (HAWORTH, PERKIN, and STEVENS), 1767.
$C_{10}H_7O_4Br$ 6-Bromo-3:4-methylenedioxycinnamic acid (HAWORTH, PERKIN, and STEVENS), 1766.
$C_{10}H_7O_6Br$ 4-Bromo-6:7-methylenedioxyhomophthalic acid (HAWORTH, PERKIN, and STEVENS), 1768.
$C_{10}H_7NBr_2$ ω-Dibromoquinaldine (HAMMICK), 1302.
$C_{10}H_8O_3N_2$ 1-Phenylbarbituric acid (MACBETH, NUNAN, and TRAILL), 1252.
$C_{10}H_8O_4S$ α- and β-Naphthylsulphuric acids, potassium salts (BURKHARDT and LAPWORTH), 689.
$C_{10}H_8NBr$ ω-Bromoquinaldine (HAMMICK), 1303.
$C_{10}H_9ON$ ω-Hydroxyquinaldine (HAMMICK), 1303.
$C_{10}H_9OCl$ Styrylacetyl chloride (LINSTEAD and WILLIAMS), 2741.
$C_{10}H_9O_3N$ β-*o*-Cyanophenylpropionic acid (EDWARDS), 816.
$C_{10}H_9O_3N$ *o*-Carboxycinnamonitrile (EDWARDS), 817.
Phthalideacetamide (EDWARDS), 816.
$C_{10}H_9O_5N$ Piperonylpyruvic acid oxime (EDWARDS), 744.
$C_{10}H_{10}OS_2$ 2-Acetyl-2-methyl-1:3-benzdithiole (HURTLEY and SMILES), 2267.
$C_{10}H_{10}O_4N_2$ Aceto-*p*-nitrobenzomethylamide (BRADY and DUNN), 2415.
$C_{10}H_{10}O_5N_2$ *ON*-Diacetyl derivatives of nitroaminophenols (HEWITT and KING), 823.
Nitro-*ON*-diacetyl-*o*-aminophenols (C. K. and E. H. INGOLD), 1321.
$C_{10}H_{10}O_6N_2$ 2-Nitro-4-acetylamino-3-methoxybenzoic acid (ROBINSON and SHINODA), 1992.
$C_{10}H_{10}O_7N_2$ 2:6-Dinitroacetyl*iso*creosol (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1974.
$C_{10}H_{11}ON$ *N*-Methylcinnamaldoxime (BRADY, DUNN, and GOLDSTEIN), 2393.
$C_{10}H_{11}O_2N$ 1-Methyl-Δ^1-*cyclo*hexenylidene-3-cyanoacetic acid, and its salts (FARMER and ROSS), 1575, 3237.
$C_{10}H_{11}O_2Cl$ Ethyl ω-chloro-*m*-tolnate (MORGAN and PORTER), 1258.
$C_{10}H_{11}O_4N$ β-*o*-Nitro-β-phenyl-α-methylhydracrylaldehyde (WILLIMOTT and SIMPSON), 2808.
$C_{10}H_{11}O_5N$ 5-Nitro-3-acetoxy-*p*-tolyl methyl ether (GULLAND and ROBINSON), 1978.
$C_{10}H_{11}O_6N$ Ethyl 3-nitro-4-methoxyphenyl carbonate (ROBINSON and SMITH), 394.
5-Nitro-2-ethoxyphenylglycollic acid, and its silver salt (CHATTAWAY), 2724.
$C_{10}H_{12}O_2S$ α-*p*-Tolylthiolpropionic acid (BROOKER and SMILES), 1726.
$C_{10}H_{12}O_4N$ 5-Nitro-2-ethoxybenzaldehyde semicarbazone, crystallography of (CHATTAWAY and CURJEL), 3214.
$C_{10}H_{12}O_4N_2$ Aceto-2-nitro-3-methoxy-*p*-toluidide (ROBINSON and SHINODA), 1992.
Nitro-*N*-methylaceto-*o*-anisidides (C. K. and E. H. INGOLD), 1324.
$C_{10}H_{12}O_4N_4$ 5-Nitro-2-ethoxybenzaldehyde semicarbazone (CHATTAWAY), 2725.
$C_{10}H_{12}O_5N_2$ 2-Nitro-6-acetylamino*iso*creosol (GULLAND and ROBINSON), 1979.
$C_{10}H_{12}O_6N_2$ Dinitro-2-propoxyanisoles (ALLAN and ROBINSON), 380.
$C_{10}H_{12}N_2S$ 1-*n*-Propylaminobenzthiazole (HUNTER), 2955.
$C_{10}H_{13}O_2N$ *N*-Methylaceto-*o*-anisidide (C. K. and E. H. INGOLD), 1323.
$C_{10}H_{13}O_2N_3$ *m*-Nitrobenzenyltrimethylamidine, hydriodide of (FORSYTH, NIMKAR, and PYMAN), 804.

$C_{10}H_{13}O_2Br$ *cyclo*Hexane*spiro*-3-bromo-Δ^2-*cyclo*penten-2-ol-4-one (ROTHSTEIN and THORPE), 2017.

$C_{10}H_{13}O_3N$ *N*-Methyl-3:4-dimethoxybenzaldoxime (BRADY, DUNN, and GOLDSTEIN), 2391.

4-Oximino-5-*cyclo*hexane*spirocyclo*penten-3-ol-1-one (HASSELL and INGOLD), 1839.

cis-Phenyl-*O*-methylserine (FORSTER and RAO), 1948.

Propane-1:3:2:4-6-keto-4-methyl-3:4:5:6-tetrahydropyridine-5-carboxylic acid (FARMER and ROSS), 3238.

$C_{10}H_{13}O_3Br$ 5-Bromo-3-methoxy-2-ethoxybenzyl alcohol (RUBENSTEIN), 651.

$C_{10}H_{13}O_4N$ 4-Nitro-5-*cyclo*hexane*spiro*-0:1:2-*bicyclo*pentene-1:3-diol (HASSELL and INGOLD), 1839.

Nitro-2-propoxyanisoles (ALLAN and ROBINSON), 380.

Nitro-4-propoxyanisoles (ROBINSON and SMITH), 398.

$C_{10}H_{13}O_5N$ 5-Nitro-3-methoxy-2-ethoxybenzyl alcohol (RUBENSTEIN), 650.

$C_{10}H_{13}N_3S$ Acetone δ-phenylthiosemicarbazone (STEPHEN and WILSON), 2534.

$C_{10}H_{14}O_3N$ 1:4-Dioximino-5-*cyclo*hexane*spirocyclo*penten-3-ol (HASSELL and INGOLD), 1839.

$C_{10}H_{15}O_2N$ *iso*Nitrosocamphor, unstable form of (FORSTER and RAO), 2670.

$C_{10}H_{15}O_2N_3$ Nitrobenzyltrimethylamines, salts of (ING and ROBINSON), 1667.

$C_{10}H_{15}O_2N_5$ 3-Propyl-1:2:4-triazole-5-azoacetylacetones (REILLY and DRUMM), 1736.

$C_{10}H_{18}O_4N$ β-Methylpimelic-β-acetic acid (FARMER and ROSS), 3239.

$C_{10}H_{16}N_{10}Cu_5$ Bisethylenediamminocupric dicuprocyanide (MORGAN and BURSTALL), 2024.

$C_{10}H_{16}IAs$ Benzyldimethylarsine methiodide (ROBERTS, TURNER, and BURY) 1445.

$C_{10}H_{19}O_2Cl$ β-Octyl chloroacetate (RULE and MITCHELL), 3207.

$C_{10}H_{19}O_2Br$ β-Octyl bromoacetate (RULE and MITCHELL), 3207.

$C_{10}H_{19}O_2I$ β-Octyl iodoacetate (RULE and MITCHELL), 3207.

$C_{10}H_{19}O_3N_3$ δ-Acetylheptoic acid semicarbazone (KON and NUTLAND), 3108.

$C_{10}H_{21}O_2N$ *n*- and *iso*-Butyl leucines, and their salts (MORGAN), 83.

10 IV

$C_{10}H_5O_2N_2Br_3$ ω-Dibromo-8-nitroquinaldine (HAMMICK), 1304.

$C_{10}H_5O_2N_2Br_3$ ω-Tribromonitroquinaldines (HAMMICK), 1303, 1304.

$C_{10}H_5O_4NCl_6$ Anhydro-5-nitro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (CHATTAWAY), 2722.

$C_{10}H_6O_2NCl$ 1-Chloro-2-nitronaphthalene (HODGSON and KILNER), 9.

$C_{10}H_6O_2NBr$ 1-Bromo-2-nitronaphthalene (HODGSON and KILNER), 9.

$C_{10}H_6O_2NI$ 1-Iodo-2-nitronaphthalene (HODGSON and KILNER), 9.

$C_{10}H_6O_3NI$ 5-Iodo-1-acetylisatin (AESCHLIMANN), 2910.

$C_{10}H_6O_3N_2Br_2$ 3:3-Dibromo-1-phenylbarbituric acid (MACBETH, NUNAN, and TRAILL), 1253.

$C_{10}H_6O_4NBr$ 4-Bromo-6:7-methylenedioxy-2-*iso*nitroso-1-hydrindone (HAWORTH, PERKIN, and STEVENS), 1768.

$C_{10}H_7O_3NCl_6$ Anhydro-5-amino-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (CHATTAWAY), 2725.

$C_{10}H_7O_3N_2Br$ 5-Bromo-1-phenylbarbituric acid (MACBETH, NUNAN, and TRAILL), 1253.

$C_{10}H_8O_3NBr$ β-6-Bromopiperonylpropionitrile (BAKER), 1075.

$C_{10}H_8O_2N_2S$ Benzylidene-3-amino-2:4-diketotetrahydrothiazole (STEPHEN and WILSON), 2538.

$C_{10}H_8O_3NBr$ Bromo-2-keto-1:2:3:4-tetrahydroquinoline-4-carboxylic acid (AESCHLIMANN), 2911.

$C_{10}H_8O_3NI$ Iodo-2-keto-1:2:3:4-tetrahydroquinoline-4-carboxylic acid (AESCHLIMANN), 2911.

$C_{10}H_8O_6N_2Cl_2$ Glycerol $\alpha\gamma$-dichlorohydrin 3:5-dinitrobenzoate (FAIRBOURNE and FOSTER), 3151.

$C_{10}H_8O_6N_2Br_2$ Dibromo-derivative of allyl 3:5-dinitrobenzoate (FAIRBOURNE and FOSTER), 3147.

$C_{10}H_8N_2Br_6S_2$ 2:6-Dimethylbenzbisthiazole hexabromide (HUNTER), 535.

$C_{10}H_9O_4NBr_2$ Glycerol $\alpha\gamma$-dibromohydrin *p*-nitrobenzoate (FAIRBOURNE and FOSTER), 3151.

Dibromo-derivative of allyl *p*-nitrobenzoate (FAIRBOURNE and FOSTER), 3147.

$C_{10}H_{10}O_3N_2S$ Methyl benziminazole-2-thioglycollate (STEPHEN and WILSON), 2536.

$C_{10}H_{10}O_3NBr$ β-6-Bromopiperonylpropionamide (BAKER), 1075.

$C_{10}H_{11}O_2NS$ *N*-*n*-Propyl-*o*-benzoicsulphinide (MCCLELLAND and GAIT), 924.

$C_{10}H_{11}O_3N_4Br$ 3-Bromo-1-phenylbarbituric acid hydrazide (MACBETH, NUNAN, and TRAILL), 1253.

$C_{10}H_{11}N_2BrS$ 5-Bromo-1-*n*-propylaminobenzthiazole (HUNTER and SOYKA), 2962.

$C_{10}H_{11}N_2Br_3S$ 5-Bromo-1-*n*-propylaminobenzthiazole dibromide (HUNTER and SOYKA), 2962.

$C_{10}H_{12}ONCl$ Phenylpropylcarbamyl chlorides (PRICE), 3230.

o-Tolylethylcarbamyl chloride (PRICE), 3231.

$C_{10}H_{13}ONI$ *N*-Methylcinnamaldoxime hydriodide (BRADY, DUNN, and GOLDSTEIN), 2397.

$C_{10}H_{12}O_2NCl$ Acetyl derivatives of chloro-3-methoxy-*o*-toluidines (GIBSON), 1426.

$C_{10}H_{12}N_2Br_2S$ 1-*n*-Propylaminobenzthiazole dibromide (HUNTER), 2955.

$C_{10}H_{12}N_2Br_4S$ 1-*n*-Propylaminobenzthiazole tetrabromide (HUNTER), 2955.

$C_{10}H_{13}ONS$ 2-Acetylamino-5-tolyl methyl sulphide (CHILD and SMILES), 2700.

$C_{10}H_{13}O_3NBr_2$ Bromopropane-$^{1:3}$II$^{2:4}$-6-keto-4-methyl-3:4:5:6-tetrahydropyridine-5-carboxylic acid (FARMER and ROSS), 3238.

$C_{10}H_{13}O_7NS$ *N*-Methyl-3:4-methylenedioxybenzaldoxime (BRADY, DUNN, and GOLDSTEIN), 2395.

$C_{10}H_{13}N_2BrS$ *s*-*p*-Bromophenyl-*n*-propylthiocarbamide (HUNTER and SOYKA), 2962.

$C_{10}H_{14}ONI$ *p*-Dimethylaminobenzaldehyde methiodide (FAIRBOURNE and WOODLEY), 3241.

$C_{10}H_{15}O_3N_4Cl$ δ-Carbethoxyanilinosemicarbazide hydrochloride (BAIRD and WILSON), 2375.

$C_{10}H_{15}O_6NS$ *N*-Methyl-*p*-methoxybenzaldoxime methosulphate (BRADY, DUNN, and GOLDSTEIN), 2395.

$C_{10}H_{18}ON_{10}Cu_4$ Aquobisethylenediamminodicupric cuprocyanide (MORGAN and BURSTALL), 2024.

$C_{10}H_{24}N_{10}S_4Cu$ Bis(triaminopropanethiocyanate)cupric thiocyanate (MANN), 2686.

10 V

$C_{10}H_{15}OBrSCd$ Thiolcamphor cadmibromide (DRUMMOND and GIBSON), 3076.

$C_{10}H_{17}O_5NSAg_2$ Silver thiolcamphor argentinitrate (DRUMMOND and GIBSON), 3075.

C_{11} Group.

$C_{11}H_{20}$ *cyclo*Hexane*spirocyclo*hexane (NORRIS), 252.

11 II

$C_{11}H_9O_2$ 1-Methyl-2-quinolone-4-carboxylic acid (AESCHLIMANN), 2908.
$C_{11}H_9N$ 4-Phenylpyridine, and its nitrates (FORSYTH and PYMAN), 2923.
$C_{11}H_{10}N_2$ Aminophenylpyridines, and their salts (FORSYTH and PYMAN), 2917.
$C_{11}H_{11}N_3$ *p*-Hydrazinophenylpyridines (FORSYTH and PYMAN), 2917.
$C_{11}H_{12}O$ δ-Phenyl-Δγ-penten-β-one (JOHNSON and KON), 2757.
$C_{11}H_{12}O_2$ Methyl β-phenyl-Δβ-butenoate (JOHNSON and KON), 2752.
β-Phenylvalerolactone (JOHNSON and KON), 2755.
$C_{11}H_{12}O_3$ *m*-Carboxybenzylacetone (MORGAN and PORTER), 2161.
Ethyl formylphenylacetate, absorption spectra of (MORTON and ROGERS), 713.
Methoxyhydroxystyryl methyl ketones (MCGOOKIN and SINCLAIR), 1579.
$C_{11}H_{12}O_5$ ω-Acetoxy-3-methoxy-4-hydroxyacetophenone (NOLAN, PRATT, and ROBINSON), 1970.
$C_{11}H_{12}O_6$ *p*-Ethylcarbonato-*m*-methoxybenzoic acid (HEAP and ROBINSON), 2343.
$C_{11}H_{14}O_2$ *p-iso*Propoxyacetophenone (BRADLEY and ROBINSON), 2362.
$C_{11}H_{14}O_3$ 3-Methoxy-5-*cyclo*hexane*spirocyclo*pentene-1:4-dione (HASSELL and INGOLD), 1840.
$C_{11}H_{16}O_7$ 4-Carboxy-2-keto*cyclo*pentylmethylsuccinic acids (INGOLD and SHOPPEE), 1916.
$C_{11}H_{14}Cl_2$ *cyclo*Hexane*spiro*-3:5-dichloro-$\Delta^{2:4}$-*cyclo*hexadiene (NORRIS), 253.
$C_{11}H_{16}O_3$ 2:3-Diethoxybenzyl alcohol (RUBENSTEIN), 650.
$C_{11}H_{17}N$ Diethylbenzylamine, nitration of (FLÜRSCHEIM and HOLMES), 1567.
$C_{11}H_{18}O$ *cyclo*Hexane*spirocyclo*hexan-3-one (NORRIS), 249.
$C_{11}H_{18}O_3$ *cyclo*Hexane-1-acetone-1-acetic acid (NORRIS), 248.
Acid, from camphorphorone and ethyl sodiocyanoacetate (KON and NUTLAND), 3109.
$C_{11}H_{18}O_4$ *cyclo*Hexane-1-acetic-1-propionic acid (NORRIS), 250.
$C_{11}H_{18}O_5$ Ethyl *cyclo*pentanol-1:2-dicarboxylate (HASSELL and INGOLD), 1469.
$C_{11}H_{19}Br$ Bromo*cyclo*hexane*spirocyclo*hexan-3-ol (NORRIS), 251.
$C_{11}H_{20}O$ *cyclo*Hexane*spirocyclo*hexan-3-ol (NORRIS), 250.
$C_{11}H_{20}O_5$ Ethyl *cyclo*pentanonedicarboxylate (INGOLD, SHOPPEE, and THORPE), 1486.
$C_{11}H_{20}O_6$ αα′-Dimethoxyazelaic acid, and its silver salt (GOSS and INGOLD), 1476.
$C_{11}H_{42}O_3$ β-Octyl methoxyacetate (RULE and MITCHELL), 3207.

11 III

$C_{11}H_7O_4N$ Nitronaphthoic acids (HARRISON and ROYLE), 89.
$C_{11}H_8O_2N_2$ Nitrophenylpyridines, and their salts (FORSYTH and PYMAN), 2916.
$C_{11}H_8N_2S$ 2-Aminonaphthathiazoles (HUNTER), 1400.
$C_{11}H_9O_2N$ Aminonaphthoic acids, and their salts (HARRISON and ROYLE), 87.
6:7-Methylenedioxy-3-methylquinoline, and its salts (WILLIMOTT and SIMPSON), 2809.
$C_{11}H_9O_4Br$ Methyl 6-bromo-3:4-methylenedioxycinnamate (HAWORTH, PERKIN, and STEVENS), 1766.
$C_{11}H_{11}ON$ 6-Methoxy-3-methylquinoline, and its salts (WILLIMOTT and SIMPSON), 2810.
$C_{11}H_{11}O_2N$ 2-Keto-1-methyl-1:2:3:4-tetrahydroquinoline-4-carboxylic acid (AESCHLIMANN), 2908
Methyl 2-keto-1:2:3:4-tetrahydroquinoline-4-carboxylate (AESCHLIMANN), 2907.
$C_{11}H_{11}O_2Br$ 2-Bromo-5:6-dimethoxy-1-hydrindone (PERKIN, RÂY, and ROBINSON), 948.

$C_{11}H_{11}O_4N$ 6-Nitro-3-methoxy-α-methylcinnamaldehyde (WILLIMOTT and SIMPSON), 2810.

$C_{11}H_{11}O_4Br$ Methyl β-6-bromopiperonylpropionate (HAWORTH, PERKIN, and STEVENS), 1766.

$C_{11}H_{11}O_6N$ Nitro-2:3-dimethoxycinnamic acids (RUBENSTEIN), 651.

$C_{11}H_{12}ON_2$ α-Cyano-γ-phenylbutyramide (LINSTEAD and WILLIAMS), 2747.

$C_{11}H_{12}OS_2$ 2-Acetonyl-2-methyl-1:3-benzdithiole (HURTLEY and SMILES), 2267.

$C_{11}H_{13}O_2N$ Methyl 1-methyl-$\Delta^{1:3}$-*cyclo*hexadienyl-3-cyanoacetate (FARMER and ROSS), 1575.

Methyl 1-methyl-Δ^1-*cyclo*hexenylidene-3-cyanoacetate (FARMER and ROSS), 1574.

$C_{11}H_{13}O_2I$ Iodo-4-hydroxymethyl*iso*propylbenzaldehydes (HENRY and SHARP), 2439.

$C_{11}H_{13}O_3N$ Aceto-*p*-methoxybenzomethylamide (BRADY and DUNN), 2416.

ON-Diacetyl-*N*-methyl-*o*-aminophenol (C. K. and E. H. INGOLD), 1327.

$C_{11}H_{13}O_4N$ β-Hydroxy-*p*-(2-carboxydimethoxyphenyl)ethylamine lactones, and their salts (EDWARDS), 745.

$C_{11}H_{14}O_5N$ β-Hydroxy-β-(2-carboxydimethoxyphenyl)ethylamines (EDWARDS), 745.

$C_{11}H_{14}O_6N_2$ 4:5-Dinitro-2-*m*-butoxyanisole (ALLAN and ROBINSON), 382.

$C_{11}H_{14}N_2S$ 1-Butylaminobenzthiazoles (HUNTER), 2956.

$C_{11}H_{13}ON_3$ *iso*Butyrophenone semicarbazone (JOHNSON and KON), 2757.

$C_{11}H_{15}OCl$ *cyclo*Hexane*spiro*-5-chloro-Δ^4-*cyclo*hexen-3-one (NORRIS), 248.

$C_{11}H_{15}O_3N$ 3-Methoxy-4-oximino-5-*cyclo*hexane*spirocyclo*pentene-1:4-dione (HASSELL and INGOLD), 1840.

Methyl 1-methyl*cyclo*hexan-3-one-1-cyanoacetate (FARMER and ROSS), 3237.

$C_{11}H_{15}O_3Br$ 5-Bromo-2:3-diethoxybenzyl alcohol (RUBENSTEIN), 651.

$C_{11}H_{15}O_4N$ Nitro-2-butoxyanisoles (ALLAN and ROBINSON), 381.

$C_{11}H_{16}O_5N$ 5-Nitro-2:3-diethoxybenzyl alcohol (RUBENSTEIN), 650.

$C_{11}H_{16}ON_4$ Acetone δ-methylanilinosemicarbazone (BAIRD and WILSON), 2373.

Acetone δ-*p*-toluidinosemicarbazone (BAIRD and WILSON), 2374.

$C_{11}H_{16}N_2S$ *s*-Phenyl-*n*-butylthiocarbamide (HUNTER), 2955.

$C_{11}H_{17}ON_3$ 2-*cyclo*Pentylidene*cyclo*pentanone semicarbazone (KON and NUTLAND), 3106.

$C_{11}H_{17}O_3N_5$ Ethyl 3-propyl-1:2:4-triazole-5-azoacetoacetates (REILLY and DRUMM), 1737.

$C_{11}H_{18}IAs$ Benzyldimethylarsine ethiodide (ROBERTS, TURNER, and BURY), 1445.

$C_{11}H_{19}ON$ Decahydro-β-naphthamides (KAY and STUART), 3038.

*cyclo*Hexane*spirocyclo*hexan-3-one oxime (NORRIS), 249.

$C_{11}H_{19}ON_3$ 2-Ethyl-2-*iso*propenyl*cyclo*pentanone semicarbazone (KON and NUTLAND), 3108.

Hexahydrobenzylideneacetone semicarbazone (KON and SMITH), 1799.

α-Δ^1-*cyclo*Hexenylmethyl ethyl ketone semicarbazone (KON and SMITH), 1797.

α-*cyclo*Hexylidenebutan-γ-one semicarbazone (KON and SMITH), 1800.

α-Methyl-Δ^1-*cyclo*hexenylacetone semicarbazone (KON and SMITH), 1796.

$C_{11}H_{19}O_3N_3$ 1-Acetyl*cyclo*hexane-1-acetic acid semicarbazone (ROTHSTEIN and THORPE), 2016.

$C_{11}H_{21}O_2N_3$ α-Hydroxy-α-*cyclo*hexylbutan-γ-one, and its semicarbazone (KON and SMITH), 1798.

$C_{11}H_{21}O_2N_3$ Acetylmethylheptoic acid semicarbazones (KON and NUTLAND), 3109.

$C_{11}H_{22}O_4N_2$ αα′-Dimethoxyazelamide (GOSS and INGOLD), 1476.

11 IV

$C_{11}H_6O_4NBr$ 6-Bromopiperonylidenecyanoacetic acid (BAKER), 1075.

$C_{11}H_8O_3NI$ Methyl 6-iodo-2-quinolone-4-carboxylate (AESCHLIMANN), 2911.

$C_{11}H_8N_2Br_4S$ 2-Aminonaphthathiazole tetrabromides (HUNTER), 1400.

$C_{11}H_{10}O_2Cl_2S$ 2:5-Dichlorophenyl acetylacetonyl sulphide (BROOKER and SMILES), 1726.

$C_{11}H_{10}O_3NI_3$ Thyroxin, tautomerism of (HICKS), 643.

$C_{11}H_{11}O_2NS$ 2:4-Diketo-3-phenyl-5-ethyltetrahydrothiazole (STEPHEN and WILSON), 2534.

$C_{11}H_{11}O_2ClS$ 4-Chlorophenyl acetylacetonyl sulphide (BROOKER and SMILES), 1726.

$C_{11}H_{11}O_4NS$ *o*-Nitrophenyl acetylacetonyl sulphide (BROOKER and SMILES), 1727.

$C_{11}H_{12}O_2N_2S$ Ethyl benziminazole-2-thioglycollate (STEPHEN and WILSON), 2536.

$C_{11}H_{13}O_2NBr$ Methyl methyl*cyclo*hexenylidenecyanoacetate dibromides (FARMER and ROSS), 1576.

$C_{11}H_{13}O_2ClHg$ 4-Hydroxy-5-chloromercuri-3-methyl-6-*iso*propylbenzaldehyde (HENRY and SHARP), 2438.

$C_{11}H_{13}N_2BrS$ 5-Bromo-1-butylaminobenzthiazoles (HUNTER and SOYKA), 2963.

$C_{11}H_{13}N_2Br_3S$ 5-Bromo-1-butylaminobenzthiazole dibromides (HUNTER and SOYKA), 2963.

$C_{11}H_{14}ONCl$ Phenylbutylcarbamyl chlorides (PRICE), 3231.

$C_{11}H_{14}N_2Br_2S$ 1-Butylaminobenzthiazole dibromides (HUNTER), 2956.

$C_{11}H_{15}N_2BrS$ *s-p*-Bromophenylbutylthiocarbamides (HUNTER and SOYKA), 2962.

C_{12} Group.

$C_{12}H_{10}$ Diphenyl, space formula of (LE FÈVRE and TURNER), 2476.

12 II

$C_{12}H_8Cl_2$ 3:4-Dichlorodiphenyl (SCARBOROUGH and WATERS), 560.

$C_{12}H_8Br_2$ 3:5-Dibromodiphenyl (SCARBOROUGH and WATERS), 561.

$C_{12}H_{10}O_2$ 5-Methoxy-α-naphthaldehyde (SHOESMITH and RUBLI), 3242.

$C_{12}H_{10}O_3$ Piperonyl ethyl ether (EDWARDS), 743.

$C_{12}H_{12}O_3$ ω:4-Diacetoxyacetophenone (NOLAN, PRATT, and ROBINSON), 1969.

$C_{12}H_{12}O_6$ *m*-Meconineacetic acid (EDWARDS), 748.

$C_{12}H_{14}O$ δ-Phenylhexen-β-ones (JOHNSON and KON), 2758.

$C_{12}H_{14}O_2$ β-*iso*Propylcinnamic acid (JOHNSON and KON), 2757.

$C_{12}H_{14}O_4$ 3-Methoxy-2-ethoxycinnamic acid (RUBENSTEIN), 652.

$C_{12}H_{15}N_5$ Benzaldehyde-3-*n*-propyl-1:2:4-triazolyl-5-hydrazone (REILLY and DRUMM), 1734.

$C_{12}H_{16}O_2$ 2-Hydroxy-5-*iso*amylbenzaldehyde (HENRY and SHARP), 2437.

$C_{12}H_{18}O_2$ 1-*cyclo*Hexyl-3:5-diketo*cyclo*hexane (KON and SMITH), 1799.

$C_{12}H_{18}O_3$ Acid, from cyano-ester $C_{13}H_{21}O_3N$ (KON and NUTLAND), 3108.

$C_{12}H_{18}O_4$ Ethylenebisacetylacetone, keto-enolic isomerism of (MORGAN and TAYLOR), 43.

Ethyl *cyclo*pentylidenemalonate (KON and SPEIGHT), 2731.

$C_{12}H_{18}O_6$ Ethyl diacetylsuccinate, absorption spectra of (MORTON and ROGERS), 713.

$C_{12}H_{20}O_6$ Di*iso*propylidenemannose, rotation and methylation of (IRVINE and SKINNER), 1089.

$C_{12}H_{22}O_{11}$ Maltose, constitution of (IRVINE and BLACK), 862; (COOPER, HAWORTH, and PEAT), 876; (HAWORTH and PEAT), 3095.

Sucrose, constitution of (MCOWAN), 1737, 1747; (HAWORTH and HIRST), 1858.

12 III

$C_{12}H_7NI_2$ Di-iodocarbazole (TUCKER), 547.

$C_{12}H_8OTe$ Phenoxtellurine, and its salts (DREW), 231.

$C_{12}H_8O_5N_2$ 3:4′-Dinitro-4-hydroxydiphenyl (BELL and KENYON), 3049.

$C_{12}H_8NCl_3$ 3:5:4′-Trichloro-4-aminodiphenyl (SCARBOROUGH and WATERS), 560.

$C_{12}H_8NBr_3$ 3:5:4′-Tribromo-4-aminodiphenyl (SCARBOROUGH and WATERS), 561.

$C_{12}H_9OCl$ 5-Methoxy-α-naphthoyl chloride (SHOESMITH and RUBLI), 3242.

$C_{12}H_9O_3N$ 4′-Nitro-4-hydroxydiphenyl (BELL and KENYON), 3049.

$C_{12}H_9O_4N$ 2-Nitro-4-phenoxyphenol (LEA and ROBINSON), 412.

$C_{12}H_9O_5N_3$ 3:5′-Dinitro-4′-amino-4-hydroxydiphenyl (HODGSON and GOROWARA), 1757.

$C_{12}H_9NCl_2$ *pp*′-Dichlorodiphenylamine (BURTON and GIBSON), 2246.

$C_{12}H_9NBr_2$ 3:5-Dibromo-4-aminodiphenyl (SCARBOROUGH and WATERS), 561.

$C_{12}H_{10}NCl$ 3-Chloro-4-aminodiphenyl, and its hydrochloride (SCARBOROUGH and WATERS), 560.

$C_{12}H_{10}NBr$ 3-Bromo-4-aminodiphenyl (KENYON and ROBINSON), 3052.
4′-Bromo-4-aminodiphenyl (SCARBOROUGH and WATERS), 560.

$C_{12}H_{10}N_2S$ 2-Methylamino-β-naphthathiazole (DYSON, HUNTER, and SOYKA), 2966.

$C_{12}H_{11}ON$ 4-Hydroxylaminodiphenyl (BELL, KENYON, and ROBINSON), 1243.

$C_{12}H_{11}O_2N$ α-Naphthylglycollamide (MCKENZIE and DENNLER), 1600.

$C_{12}H_{11}O_3N$ 2-Cyano-5:6-dimethoxy-1-hydrindone (PERKIN, RÂY, and ROBINSON), 948.
Methyl 1-methyl-2-quinolone-4-carboxylate (AESCHLIMANN), 2908.

$C_{12}H_{11}O_5N$ 2-Carboxy-5- and -7-methoxyindole-3-acetic acids (PERKIN and RUBENSTEIN), 361.

$C_{12}H_{11}O_5N_3$ Meconineacetyl azide (EDWARDS), 746.

$C_{12}H_{13}O_6N_3$ Triacetyl derivative of 5-nitro-2-aminophenol (HEWITT and KING), 823.

$C_{12}H_{13}O_2N$ 6:7-Dimethoxy-3-methylquinoline, and its hydrochloride (WILLIMOTT and SIMPSON), 2810.

$C_{12}H_{13}O_3N$ Meconineacetamide (EDWARDS), 745.
6-Nitro-3:4-dimethoxy-α-methylcinnamaldehyde (WILLIMOTT and SIMPSON), 2810.

$C_{12}H_{13}O_6N$ 5-Nitro-3-methoxy-2-ethoxycinnamic acid (RUBENSTEIN), 652.

$C_{12}H_{13}O_7N$ Acetyl-5-nitro-2-ethoxyphenylglycollic acid (CHATTAWAY), 2724.

$C_{12}H_{14}ON_4$ 5-Salicylideneamino-3-*n*-propyl-1:2:4-triazole (REILLY and DRUMM), 1733.

$C_{12}H_{14}O_2S$ *p*-Tolyl acetylacetonyl sulphide (BROOKER and SMILES), 1726.

$C_{12}H_{14}O_5N_2$ Nitroso-β-hydroxy-β-(2-carboxy-3-4-dimethoxyphenyl)ethylmethylamine lactone (EDWARDS), 747.

$C_{12}H_{14}NI$ 3-Methylquinoline ethiodide (WILLIMOTT and SIMPSON), 2809.

$C_{12}H_{14}NI_3$ *p*-Toluquinaldine methiodide periodide (HUMPHRIES), 375.

$C_{12}H_{15}ON$ β-Phenyl-γ-methyl-Δβ-pentenoamide (JOHNSON and KON), 2757.
β-Phenyl-Δβ-hexenoamide (JOHNSON and KON), 2755.
Anilide of acid, $C_7H_{10}O_4$ (KON and SPEIGHT), 2730.

$C_{12}H_{15}ON_3$ δ-Phenyl-Δγ-penten-β-one semicarbazone (JOHNSON and KON), 2757.
Styrylacetone semicarbazone (LINSTEAD and WILLIAMS), 2744.

$C_{12}H_{15}O_2N$ Methyl 1-methyl-Δ1.3-*cyclo*hexadienyl-3-α-cyanopropionate (FARMER and ROSS), 1576.

$C_{12}H_{15}O_4N_3$ 2:4-Dinitro-*m*-tolylpiperidine (GORNALL and ROBINSON), 1984.

$C_{12}H_{16}O_3N_4$ 4-Nitro-*o*-anisidine diazopiperidide (HOLMES and INGOLD), 1331.

$C_{12}H_{14}O_3Hg$ 2-Acetoxymercuri-*p-tert.*-butylphenol (HENRY and SHARP), 2435.
Acetoxymercuricarvacrol (HENRY and SHARP), 2436.
$C_{12}H_{16}N_2S$ 1-Amylaminobenzthiazoles (HUNTER), 2956.
$C_{12}H_{17}ON_3$ *o*-Anisidine diazopiperidide (HOLMES and INGOLD), 1329.
$C_{12}H_{17}O_3N$ Ethyl 1-methyl*cyclo*hexan-3-one-1-cyanoacetate (FARMER and ROSS), 3237.
$C_{12}H_{17}O_4N$ 4-Nitro-1:3-dimethoxy-5-*cyclo*hexane-0:1:2-*spirocyclo*pentene (HASSELL and INGOLD), 1840.
$C_{12}H_{17}O_5N$ *β*-Hydroxy-*β*-(2-carboxydimethoxyphenyl)ethylmethylamines (EDWARDS), 749.
$C_{12}H_{18}ON_4$ Diethyl ketone *δ*-anilinosemicarbazone (BAIRD and WILSON), 2371.
$C_{12}H_{18}O_2N_2$ Nitrosoamine from base $C_{12}H_{19}ON$ (BANFIELD and KENYON), 1628.
$C_{12}H_{18}O_3N_4$ Methyl 1-methyl*cyclo*hexan-3-one-1-cyanoacetate semicarbazone (FARMER and ROSS), 3237.
$C_{12}H_{18}N_2S$ *s*-Phenyl-*n*-amylthiocarbamide (HUNTER), 2956.
$C_{12}H_{18}IAs$ *As*-Methyltetrahydroarsindole ethiodide (ROBERTS, TURNER, and BURY), 1444.
$C_{12}H_{19}ON$ Base from reduction of $C_{18}H_{22}O_2N_2$ (BANFIELD and KENYON), 1628.
Substance, from pulegone and ethyl sodiocyanoacetate (KON and NUTLAND), 3110.
$C_{12}H_{20}O_4Br_2$ Ethyl *aa'*-dibromosuberate (GOSS and INGOLD), 1473.
$C_{12}H_{21}ON_3$ 2:5-Dimethyl-2-*iso*propenyl*cyclo*hexanone semicarbazone (KON and NUTLAND), 3110.
*cyclo*Hexane-1-acetone-1-acetic acid semicarbazone (NORRIS), 248.
*cyclo*Hexane*spirocyclo*hexan-3-one semicarbazone (NORRIS), 249.
5-Methyl-2-ethyl-2-*iso*propenyl*cyclo*pentanone semicarbazone (KON and NUTLAND), 3109.
$C_{12}H_{22}O_4N_4$ Ethylenebisacetylacetone tetraoximes (MORGAN and TAYLOR), 48.
$C_{12}H_{24}O_2N_4$ Hexahydrobenzylideneacetone semicarbazide-semicarbazone (KON and SMITH), 1799.

12 IV

$C_{12}H_6ONBr_3$ 3:4:4'-Tribromo-2'-nitrodiphenyl (LE FÈVRE and TURNER), 2043.
$C_{12}H_6O_4N_2Cl_2$ 4:4'-Dichlorodinitrodiphenyls, isomeric (HODGSON and GOROWARA), 1754.
$C_{12}H_6O_4N_2I_2$ 4:4'-Di-iododinitrodiphenyls (HODGSON), 2385.
$C_{12}H_6O_6N_3Br$ 4-Bromo-2':3':4'-trinitrodiphenyl (LE FÈVRE and TURNER), 2044.
$C_{12}H_6O_{11}N_4Te$ 2:8-Dinitrophenoxtellurine 10:10-dinitrate (DREW), 3065.
$C_{12}H_7O_2NCl_2$ 4:4'-Dichloro-2-nitrodiphenyl (LE FÈVRE and TURNER), 2045.
$C_{12}H_7O_2NBr_2$ 4:4'-Dibromo-2-nitrodiphenyl (DENNETT and TURNER), 479.
4:4'-Dibromo-3-nitrodiphenyl (LE FÈVRE and TURNER), 2046.
$C_{12}H_7O_2NI_2$ 4:4'-Di-iodo-2-nitrodiphenyl (HODGSON), 2385.
$C_{12}H_7O_9N_3Te$ 2-Nitrophenoxtellurine 10:10-dinitrate (DREW), 3065.
$C_{12}H_7NCl_3As$ 2:8:10-Trichloro-5:10-dihydrophenarsazine (BURTON and GIBSON), 2246.
$C_{12}H_8OCl_2Te$ 10:10-Dichlorophenoxtellurine (DREW), 230.
$C_{12}H_8O_4N_2Cl$ 4-Chloro-2:3'-dinitro-4'-aminodiphenyl (LE FÈVRE and TURNER), 2048.
4-Chloro-3:3'-dinitro-4'-aminodiphenyl (HODGSON and GOROWARA), 1757.
$C_{12}H_8O_4N_2Br$ 4-Bromo-2:3'-dinitro-4'-aminodiphenyl (LE FÈVRE and TURNER), 2048.
$C_{12}H_8O_7N_2Te$ Phenoxtellurine 10:10-dinitrate (DREW), 3065.

$C_{12}H_8NCl_4As$ Dichloro-5:10-dihydrophenarsazines (BURTON and GIBSON), 2246.
$C_{12}H_8ClSAs$ 10-Chlorophenthiarsine (ROBERTS and TURNER), 1209.
$C_{12}H_8OCl_3Te$ *p*-Phenoxyphenyltelluritrichloride (DREW), 227.
$C_{12}H_9OSAs$ *o*-Phenylthiolphenylarsenious oxide (ROBERTS and TURNER), 1208.
$C_{12}H_9O_2N_2Br$ 4-Bromo-3′-nitro-4′-aminodiphenyl (LE FÈVRE and TURNER), 2045.
$C_{12}H_9O_3NCl_4$ Acetylanhydro-5-amino-2-*βββ*-trichloro-*a*-hydroxyethoxy-1-*βββ*-trichloro-*a*-hydroxyethylbenzene (CHATTAWAY), 2726.
$C_{12}H_9O_4NS_2$ Benzene-*o*-disulphonphenylimide (HURTLEY and SMILES), 1825.
$C_{12}H_9O_4N_2As$ Nitrophenarsazinic acid, salts of (BURTON and GIBSON), 2245.
$C_{12}H_9O_{10}N_2Te$ 4:8-Dinitro-10-hydroxyphenoxtellurine 10-nitrate hydrate (DREW), 3065.
$C_{12}H_9NClAs$ 10-Chloro-5:10-dihydrophenarsazine (BURTON and GIBSON), 450, 464.
$C_{12}H_9Cl_2SAs$ *o*-Phenylthiolphenyldichloroarsine (ROBERTS and TURNER), 1208.
$C_{12}H_{10}O_3NI$ Ethyl 6-iodo-3-quinolone-4-carboxylate (AESCHLIMANN), 2911.
$C_{12}H_{10}O_8N_2Te$ 4-Nitro-10-hydroxyphenoxtellurine 10-nitrate hydrate (DREW), 3065.
$C_{12}H_{10}N_2Br_6S$ 2-Methylamino-*β*-naphthathiazole hexabromide (DYSON, HUNTER, and SOYKA), 2966.
$C_{12}H_{11}ONI$ 6-Methoxy-3-methylquinoline methiodide (WILLIMOTT and SIMPSON), 2811.
$C_{12}H_{11}O_3NS$ 1-Acetylaminonaphthalene-4-sulphinic acid (CHILD and SMILES), 2701.
$C_{12}H_{11}O_3SAs$ *o*-Phenylthiolphenylarsinic acid (ROBERTS and TURNER), 1208.
$C_{12}H_{11}N_2Cl_3As$ 10-Chloro-1-amino-5:10-dihydrophenarsazine hydrochloride (BURTON and GIBSON), 2245.
$C_{12}H_{12}O_3NI$ 6:7-Methylenedioxy-3-methylquinoline methiodide (WILLIMOTT and SIMPSON), 2809.
$C_{12}H_{12}O_3NI$ Ethyl iodo-2-keto-1:2:3:4-tetrahydroquinoline-4-carboxylate (AESCHLIMANN), 2911.
$C_{12}H_{12}O_3NAs$ Diphenylamine-*p*-arsinic acid (BURTON and GIBSON), 461.
$C_{12}H_{12}O_6S_2As_2$ Diphenyl sulphide *pp′*-diarsinic acid (HEWITT, KING, and MURCH), 1369.
$C_{12}H_{13}ON_2S$ 2:4-Diketo-3-phenyltetrahydrothiazole-2-*iso*propylidenehydrazone (STEPHEN and WILSON), 2534.
$C_{12}H_{15}N_2BrS$ 5-Bromo-1-amylaminobenzthiazoles (HUNTER and SOYKA), 2963.
$C_{12}H_{15}N_2Br_3S$ 5-Bromo-1-*iso*amylaminobenzthiazole dibromide (HUNTER and SOYKA), 2963.
$C_{12}H_{15}N_2Br_5S$ 5-Bromo-1-*n*-amylaminobenzthiazole tetrabromide (HUNTER and SOYKA), 2963.
$C_{12}H_{16}ONCl$ *β-p*-Chloroanilino-*β*-methylpentan-3-one (BANFIELD and KENYON), 1624.
Phenyl*iso*amylcarbamyl chloride (PRICE), 3231.
$C_{12}H_{16}O_{13}S_2Te$ Phenoxtellurine dibisulphate trihydrate (DREW), 3070.
$C_{12}H_{17}O_3N_2I$ *m*-Nitrobenzylpiperidine hydriodide (ING and ROBINSON), 1664.
$C_{12}H_{17}N_2BrS$ *s-p*-Bromophenylamylthiocarbamides (HUNTER and SOYKA), 2963.
$C_{12}H_{17}N_2Br_3S$ 1-Amylaminobenzthiazole dibromide hydrobromides (HUNTER), 2956.
$C_{12}H_{18}ON_2Cl$ *cyclo*Hexane*spiro*-5-chloro-Δ^4-*cyclo*hexen-3-one semicarbazone (NORRIS), 249.
$C_{12}H_{18}O_2N_2Pd$ Palladous ethylenediaminobisacetylacetone (MORGAN and SMITH), 921.

$C_{12}H_{20}O_5N_2Cu$ Aquo-cupric ethylenediaminobisacetylacetone (MORGAN and SMITH), 918.

$C_{12}H_{44}N_{12}I_6Cu_3$ Tetratriaminopropanetricupric hexaiodide (MANN), 2685.

12 V

$C_{12}H_6O_6N_2I_2As_2$ 5:5′-Di-iodo-3:3′-dinitro-4:4′-dihydroxyarsenobenzene (MACALLUM), 1647.

$C_{12}H_9O_4NBrAs$ 2-Bromo-6′-nitrodiphenylarsinic acid (BURTON and GIBSON), 457.

$C_{12}H_{10}O_9N_2SAs$ 3:3′-Dinitrobenzenesulphonyl-4-aminophenylarsinic acid (HEWITT, KING, and MURCH), 1364.

$C_{12}H_{11}O_3NBrAs$ 2-Bromo-6′-aminodiphenylarsinic acid (BURTON and GIBSON), 457.

$C_{12}H_{11}O_7N_2SAs$ 3′-Nitrobenzenesulphonyl-4-aminophenylarsinic acid (HEWITT, KING, and MURCH), 1364.

$C_{12}H_{11}O_9N_2SAs$ 3′-Nitrobenzenesulphonylaminohydroxyphenylarsinic acids (HEWITT, KING, and MURCH), 1365.

$C_{12}H_{13}O_5N_2SAs$ 3′-Aminobenzenesulphonyl-4-aminophenylarsinic acid, and its salts (HEWITT, KING, and MURCH), 1364.

$C_{12}H_{13}O_6NSAs$ 3′-Aminobenzenesulphonylaminohydroxyphenylarsinic acids (HEWITT, KING, and MURCH), 1366.

$C_{12}H_{14}O_5N_2SAs$ 3:3′-Diaminobenzenesulphonyl-4-aminophenylarsinic acid (HEWITT, KING, and MURCH), 1365.

C_{13} Group.

$C_{13}H_{10}$ Fluorene, absorption spectrum of (CAPPER and MARSH), 724.

$C_{13}H_{14}$ Substance, from dehydrogenation of tetra*cyclo*squalene (HARVEY, HEILBRON, and KAMM), 3138.

13 II

$C_{13}H_{10}O_2$ 4-Hydroxyaldehydodiphenyl (BELL and KENYON), 3047.

$C_{13}H_{10}S_2$ 2-Phenyl-1:3-benzdithiole (HURTLEY and SMILES), 1827.

$C_{13}H_{12}O_2$ Methoxydiphenyl ethers (LEA and ROBINSON), 412.

$C_{13}H_{12}N_2$ Diaminofluorenes (MORGAN and THOMASON), 2694.

$C_{13}H_{14}O_2$ 3:5-Diketo-1-benzyl*cyclo*hexane (LINSTEAD and WILLIAMS), 2745.

$C_{13}H_{14}O_4$ 3-*m*-Carboxybenzylacetylacetone, and its copper salt (MORGAN and PORTER), 1259.

3-Methoxy-2-acetoxystyryl methyl ketone (MCGOOKIN and SINCLAIR), 1580.

$C_{15}H_{14}O_5$ ω:4-Diacetoxy-3-methoxyacetophenone (NOLAN, PRATT, and ROBINSON), 1970.

$C_{13}H_{16}O$ Methyl β-phenyl-Δ^{β}-hexenoate (JOHNSON and KON), 2756.

$C_{13}H_{16}O_2$ Ethyl β-phenyl-Δ^{β}-pentenoate (JOHNSON and KON), 2754.

$C_{13}H_{16}O_4$ 2:3-Diethoxycinnamic acid (RUBENSTEIN), 652.

$C_{13}H_{16}N_2$ 1-*p*-Toluidino-1-cyano*cyclo*pentane (OAKESHOTT and PLANT), 1211.

$C_{13}H_{17}N$ Octahydroacridine, and its salts (PERKIN and SEDGWICK), 438.

$C_{13}H_{18}O_4$ Ethyl 1:3-diketodecahydronaphthalene-4-carboxylate (KON and QUDRAT-I-KHUDA), 3071.

$C_{13}H_{16}O_{12}$ Tetracarbomethoxy-*l*-arabinose (HAWORTH and MAW), 1752.

Tetracarbomethoxy-*l*-xylose (HAWORTH and MAW), 1754.

$C_{13}H_{20}O_4$ Ethyl Δ^1-*cyclo*hexenylmalonate (KON and SPEIGHT), 2733.

Ethyl ester of acid, $C_9H_{12}O_4$ (KON and SPEIGHT), 2732.

$C_{13}H_{24}O_2$ Ethyl *sec.*-butyl*iso*valerylacetate (JONES), 2769.

$C_{13}H_{24}O_6$ Ethyl αα′-dihydroxyazelate (GOSS and INGOLD), 1476.

Ethyl αα′-dimethoxypimelate (HASSELL and INGOLD), 1469.

$C_{13}H_{24}O_{11}$ Methylmaltoside (IRVINE and BLACK), 874.

13 III

$C_{13}H_8O_5N_2$ Dinitrofluorenones (Morgan and Thomason), 2694.
$C_{13}H_8O_2Cl_2$ 3:5-Dichlorophenyl benzoate (Hodgson and Wignall), 2078.
$C_{13}H_8O_2Br_2$ 3:5-Dibromophenyl benzoate (Hodgson and Wignall), 2078.
$C_{13}H_8O_2I_2$ 3:5-Di-iodophenyl benzoate (Hodgson and Wignall), 2078.
$C_{13}H_8O_4N_2$ Dinitrofluorenes (Morgan and Thomason), 2693.
$C_{13}H_8N_4Br_2$ 1-(2:4-Dibromophenyl)-4-phenyltetrazole (Chattaway and Parkes), 114.
$C_{13}H_9O_3N$ Benzoylfurfuraldehydecyanohydrin (Greene), 330.
$C_{13}H_9NI_2$ 3:6-Di-iodo-9-methylcarbazole (Tucker), 552.
$C_{13}H_9N_5Br_2$ 1-(2:4-Dibromophenyl)-5-phenyl-1:4-dihydropentazine (Chattaway and Parkes), 116.
$C_{13}H_9ClS_2$ 2-Phenyl-1:3-benzdithiole-1-sulphonium chloride (Hurtley and Smiles), 1827.
$C_{13}H_9Br_2S_2$ 2-Phenyl-1:3-benzdithiole-1-sulphonium perbromide (Hurtley and Smiles), 1828.
$C_{13}H_{10}O_5N_2$ Dinitro-4-methoxydiphenyls (Bell and Kenyon), 3048.
$C_{13}H_{10}O_5N_4$ Dinitro-4-nitrosomethylaminodiphenyl (Bell and Kenyon), 2710.
$C_{13}H_{10}N_2S$ Thiocarbonylbenzidine, and its sulphate (Le Fèvre and Turner), 2483.
$C_{13}H_{11}O_3N$ Nitro-4-methoxydiphenyls (Bell and Kenyon), 3048.
$C_{13}H_{11}O_4N$ 3-Nitro-6-methoxydiphenyl ether (Lea and Robinson), 412.
$C_{13}H_{11}O_4N_3$ Dinitro-4-methylaminodiphenyl (Bell and Kenyon), 2710.
$C_{13}H_{11}O_9N_5$ Nitrobenzylammonium picrates (Goss, Ingold, and Wilson), 2455.
$C_{13}H_{11}N_2F$ Fluorobenzaldehyde phenylhydrazones (Shoesmith, Sosson, and Slater), 2761.
$C_{13}H_{12}ON_2$ 4-Nitrosomethylaminodiphenyl (Bell, Kenyon, and Robinson), 1245.
$C_{13}H_{12}N_2S$ 2-Ethylamino-β-naphthathiazole (Dyson, Hunter, and Soyka), 2966.
$C_{13}H_{12}N_4Br_2$ ω-Hydrazinobenzaldehyde-2:4-dibromophenylhydrazone (Chattaway and Parkes), 115.
$C_{13}H_{13}ON$ 2-*p*-Ethoxyphenylpyridine, and its picrate (Forsyth and Pyman), 2918.
$C_{13}H_{13}O_2N$ Tetrahydrocarbazolecarboxylic acids, and their salts (Collar and Plant), 809.
$C_{13}H_{13}O_2N_3$ 1-Methyl-Δ^1-*cyclo*hexene-3:3-dicyanoacetimide, and its ammonium salt (Farmer and Ross), 1577.
$C_{13}H_{13}O_3As$ Phenylbenzylarsinic acid, salts of (Roberts, Turner, and Bury), 1447.
$C_{13}H_{14}O_2N_2$ 5-Nitro-6-methyltetrahydrocarbazole (Manjunath and Plant), 2262.
$C_{13}H_{15}ON$ 11-Hydroxy-6-methyltetrahydrocarbazolenine (Manjunath and Plant), 2262.
$C_{13}H_{15}O_4N$ Ethyl 5:6-dimethoxyindole-2-carboxylate (Perkin and Rubenstein), 360.
$C_{13}H_{15}O_5N$ β-Acetoxy-β-(2-carboxy-3:4-dimethoxyphenyl)ethylamine lactone (Edwards), 746.
Aminoguaiacols (Oxford), 2007.
Triacetylaminoguaiacol (Oxford), 2007.
$C_{13}H_{15}O_6N$ Ethyl nitro-2:3-dimethoxycinnamates (Rubenstein), 651.
$C_{13}H_{16}O_2N_2$ *cyclo*Hexanonecarboxyphenylhydrazones (Collar and Plant), 809.
$C_{13}H_{16}O_2N_4$ 1-Methyl-Δ^1-*cyclo*hexene-3:3-dicyanoacetamide (Farmer and Ross), 1577.

$C_{13}H_{16}O_4Hg$ 3-Acetoxymercuri-4-hydroxy-2-methyl-5-*iso*propylbenzaldehyde (HENRY and SHARP), 2439.

2-Hydroxy-3-acetoxymercuri-5-*tert.*-butylbenzaldehyde (HENRY and SHARP), 2437.

4-Hydroxy-5-acetoxymercuri-3-methyl-6-*iso*propylbenzaldehyde (HENRY and SHARP), 2439.

$C_{13}H_{17}ON_3$ Phenylhexenone semicarbazones (JOHNSON and KON), 2758.

$C_{13}H_{17}O_2N$ 1-*p*-Toluidino*cyclo*pentane-1-carboxylic acid (OAKESHOTT and PLANT), 1211.

$C_{13}H_{18}ON_4$ *cyclo*Hexanone δ-anilinosemicarbazone (BAIRD and WILSON), 2371.

$C_{13}H_{18}O_5Hg$ 2-Acetoxymercuri-*p*-*iso*amylphenol (HENRY and SHARP), 2436.

$C_{13}H_{18}N_2S$ 1-*n*-Hexylaminobenzthiazole (HUNTER), 2957.

$C_{13}H_{19}O_2N$ Substance, from α-phenyl-γ-ethyl-Δ$^{\beta}$-penten-α-one and hydroxylamine hydrochloride (FARROW and KON), 2137.

$C_{13}H_{19}O_2N_3$ 2-Hydroxy-5-*iso*amylbenzaldehyde semicarbazone (HENRY and SHARP), 2438.

$C_{13}H_{19}O_3N$ Substance, from 2-*iso*propylidene*cyclo*pentanone and ethyl sodiocyanoacetate (KON and NUTLAND), 3108.

$C_{13}H_{20}ON_4$ Methyl *tert.*-butyl ketone δ-anilinosemicarbazone (BAIRD and WILSON), 2371.

$C_{13}H_{20}O_2N_2$ α-Phenyl-γ-ethyl-Δ$^{\beta}$-penten-α-one oximino-oxime (FARROW and KON), 2137.

$C_{13}H_{20}O_3N_4$ Ethyl 1-methyl*cyclo*hexan-3-one-1-cyanoacetate semicarbazone (FARMER and ROSS), 3237.

$C_{13}H_{20}N_2S$ *s*-Phenyl-*n*-hexylthiocarbamide (HUNTER), 2957.

$C_{13}H_{21}ON_3$ Allyl-Δ^1-*cyclo*hexenylacetone semicarbazone (KON and SMITH), 1797.

2-Ethyl-2-Δ^1-*cyclo*pentenyl*cyclo*pentanone semicarbazone (KON and NUTLAND), 3107.

2-Δ^1-*cyclo*Hexenyl*cyclo*hexanone semicarbazone (KON and NUTLAND), 3104.

$C_{13}H_{22}IAs$ δ-Phenyl-*n*-butyldimethylarsine methiodide (ROBERTS, TURNER, and BURY), 1445.

γ-Phenylpropyldimethylethylarsonium iodide (ROBERTS, TURNER, and BURY), 1444.

$C_{13}H_{23}ON_3$ Ethyl-α-Δ^1-*cyclo*hexenylmethylethyl ketone semicarbazone (KON and SMITH), 1797.

5-Methyl-2-ethyl-2-*iso*propenyl*cyclo*hexanone semicarbazone (KON and NUTLAND), 3110.

Propyl-Δ^1-*cyclo*hexenylacetone semicarbazone (KON and SMITH), 1796.

$C_{13}H_{24}IAs$ δ-Phenyl-*n*-butyldimethylarsine ethiodide (ROBERTS, TURNER, and BURY), 1445.

13 IV

$C_{13}H_6N_2Cl_6S$ 5-Di-3:4:5-trichlorophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 3043.

$C_{13}H_7O_2N_5Br_2$ 1-(2:4-Dibromophenyl)-4-*m*-nitrophenyl-1:2:3:5-tetrazole (CHATTAWAY and PARKES), 114.

$C_{13}H_8O_3N_3Cl_3$ 2:4:6-Trichloro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone (HODGSON and BEARD), 153.

$C_{13}H_8O_4NCl$ 3-Chloro-5-nitrophenyl benzoate (HODGSON and WIGNALL), 2077.

$C_{13}H_8O_4NBr$ 3 Bromo-2-nitrophenyl benzoate (HODGSON and MOORE), 158.

$C_{13}H_8O_4NI$ 3-Iodo-5-nitrophenyl benzoate (HODGSON and WIGNALL) 2077.

$C_{13}H_8O_5N_4Cl_2$ Dichloronitro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and BEARD), 2035.

$C_{13}H_9O_7N_3Cl$ Chlorodinitro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and BEARD), 2035.

$C_{13}H_8NBr_4S$ 5-Bromo-1-phenylbenzthiazole tetrabromide (HUNTER), 540.

$C_{13}H_8N_2Cl_4S$ *s*-Di-2:3-dichlorophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 3042.

$C_{13}H_9ONS$ 2-Keto-1-phenyl-1:2-dihydrobenz*iso*thiazole (McCLELLAND and GAIT), 923.

$C_{13}H_9O_3N_2Cl_3$ Dichloro-3-hydroxybenzaldehydephenylhydrazones (HODGSON and BEARD), 152.

$C_{13}H_9O_5N_4Cl$ Chloronitro-3-hydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and BEARD), 2032.

$C_{13}H_9NBr_4S$ 1-Phenylbenzthiazole tetrabromide (HUNTER), 539.

$C_{13}H_{10}O_2N_2F$ Fluorobenzaldehyde *p*-nitrophenylhydrazones (SHOESMITH, SOSSON, and SLATER), 2761.

$C_{13}H_{10}O_2N_2Cl$ Chloro-*m*-hydroxybenzaldehyde phenylhydrazones (HODGSON and BEARD), 150.

$C_{13}H_{10}O_8N_3As$ 3′:5-Dinitrobenzoyl-4-amino-2-hydroxyphenylarsinic acid (HEWITT and KING), 825.

$C_{13}H_{10}N_2Br_4S$ 5-Amino-1-phenylbenzthiazole tetrabromide (HUNTER), 541.

$C_{13}H_{11}O_7N_2As$ Nitrobenzoylaminohydroxyphenylarsinic acids, and their salts (HEWITT and KING), 824.

$C_{13}H_{11}O_5N_2As$ Nitrohydroxybenzoylaminohydroxyphenylarsinic acids (HEWITT and KING), 827.

$C_{13}H_{11}NClAs$ 10-Chloro-2-methyl-5:10-dihydrophenarsazine (BURTON and GIBSON), 468.

$C_{13}H_{11}OClAs$ *o*-Phenoxyphenylmethylchloroarsine (ROBERTS and TURNER), 1209.

$C_{13}H_{12}O_2NAs$ 2-Methylphenarsazinic acid, and its salts (BURTON and GIBSON), 469.

$C_{13}H_{13}N_2Br_4S$ 2-Ethylamino-β-naphthathiazole tetrabromide (DYSON, HUNTER, and SOYKA), 2967.

$C_{13}H_{13}ONS$ *dl*-4′-Amino-4-methyldiphenyl sulphoxide (HARRISON, KENYON, and PHILLIPS), 2085.

$C_{13}H_{13}O_2N_4I$ Substance, from α-picoline methiodide and *p*-nitrophenylnitrosoamine (HUMPHRIES), 376.

$C_{13}H_{13}O_6N_2As$ 3′-Aminobenzoyl-3-amino-4-hydroxyphenylarsinic acid, and its salts (HEWITT and KING), 828.

$C_{13}H_{13}O_6N_2As$ Aminohydroxybenzoylaminohydroxyphenylarsinic acids and their salts (HEWITT and KING), 827.

$C_{13}H_{14}O_5N_2As$ 3′:5-Diaminobenzoyl-4-amino-2-hydroxyphenylarsinic acid, and its salts (HEWITT and KING), 825.

$C_{13}H_{17}N_2BrS$ 5-Bromo-1-*n*-hexylaminobenzthiazole (HUNTER and SOYKA), 2964.

$C_{13}H_{17}N_2Br_3S$ 5-Bromo-1-*n*-hexylaminobenzthiazole dibromide (HUNTER and SOYKA), 2964.

$C_{13}H_{18}N_2Br_2S$ 1-*n*-Hexylaminobenzthiazole dibromide (HUNTER), 2957.

$C_{13}H_{19}N_2BrS$ *s*-*p*-Bromophenyl-*n*-hexylthiocarbamide (HUNTER and SOYKA), 2964.

13 V

$C_{13}H_8O_2N_2Br_2S$ 5-Nitro-1-phenylbenzthiazole dibromide (HUNTER), 540.

$C_{13}H_{13}O_9N_3SAs$ 3:3′-Dinitro-4′-toluenesulphonyl-4-aminophenylarsinic acid (HEWITT, KING, and MURCH), 1363.

$C_{13}H_{13}O_2NBrAs$ 2-Bromo-6′-methylaminodiphenylarsinic acid (BURTON and GIBSON), 458.

$C_{13}H_{13}O_3N_2SAs$ 3′-Amino-4′-toluenesulphonyl-4-aminophenylarsenious oxide (HEWITT, KING, and MURCH), 1362.

$C_{13}H_{13}O_7N_2AsS$ 3′-Nitro-4′-toluenesulphonyl-4-aminophenylarsinic acid (HEWITT, KING, and MURCH), 1361.

$C_{13}H_{14}O_3N_2SAs$ 3:3′-Diamino-4′-toluenesulphonyl-4-aminophenylarsenious oxide (HEWITT, KING, and MURCH), 1364.

$C_{13}H_{15}O_5N_2SAs$ 3′-Amino-4′-toluenesulphonyl-4-aminophenylarsinic acid, and its salts (HEWITT, KING, and MURCH), 1361.

$C_{13}H_{16}O_5N_2SAs$ 3:3′-Diamino-4′-toluenesulphonyl-4-aminophenylarsinic acid, and its magnesium salt (HEWITT, KING, and MURCH), 1363.

C_{14} Group.

$C_{14}H_{10}$ Anthracene, absorption spectrum of (CAPPER and MARSH), 724.
Phenanthrene, absorption spectrum of (CAPPER and MARSH), 724.

14 II

$C_{14}H_8O_2$ Quinizarin, action of thionyl chloride on (GREEN), 1428.

$C_{14}H_8S_4$ 2:2′-Bis-1:3-benzdithiolene (HURTLEY and SMILES), 2263.

$C_{14}H_{11}N$ 1-Methyl-β-naphthaquinoline, and its picrate (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2256.

$C_{14}H_{12}O$ γ-Ketobutenylnaphthalenes (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2257.

$C_{14}H_{12}O_5$ 2:4:6-Trihydroxyphenyl *p*-hydroxybenzyl ketone ($+H_2O$) (BAKER and ROBINSON), 2716.

$C_{14}H_{12}N_2$ 3:4′-Diaminotolane (HARRISON), 1237.

$C_{14}H_{12}S_2$ 2-Phenyl-2-methyl-1:3-benzdithiole (HURTLEY and SMILES), 1827.

$C_{14}H_{13}N$ Methyldihydronaphtha*iso*quinolines, and their picrates (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2258.

$C_{14}H_{14}O$ γ-Ketobutylnaphthalenes (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2258.

$C_{14}H_{14}N_2$ 3:4′-Diaminostilbene (HARRISON), 1236.

$C_{14}H_{15}N$ Methyltetrahydroacridine, and its picrate (PERKIN and SEDGWICK), 443.
Methyl-1:2:3:4-tetrahydronaphthaquinolines, and their salts (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2252.

$C_{14}H_{16}O$ α-Δ¹-*cyclo*Hexenylacetophenone (FARROW and KON), 2132.

$C_{14}H_{16}O_2$ 1-α-Naphthyl-2:2-dimethylethylene glycol (MCKENZIE and DENNLER), 1601.

$C_{14}H_{16}O_5$ Ethyl 5:6-dimethoxy-1-hydrindone-2-carboxylate (PERKIN, RÂY, and ROBINSON), 949.

$C_{14}H_{16}O_6$ Ethyl *m*-meconineacetate (EDWARDS), 748.

$C_{14}H_{17}N$ 3:6-Dimethyltetrahydrocarbazole (OAKESHOTT and PLANT), 1213.

$C_{14}H_{19}N$ Methyloctahydroacridines (PERKIN and SEDGWICK), 444.

$C_{14}H_{20}O_{10}$ Tetra-acetylglucose, mutarotation of (JONES and LOWRY), 720.

$C_{14}H_{22}O_4$ Ethyl ester, from acid, $C_{10}H_{14}O_4$ (KON and SPEIGHT), 2734.

$C_{14}H_{22}N_2$ *n*-Heptaldehyde methylphenylhydrazone (BAIRD and WILSON), 2374.

$C_{14}H_{26}O_2$ 4-Ketomyristic acid (G. M. and R. ROBINSON), 2206.

14 III

$C_{14}H_5O_8N_3$ 2:4:7-Trinitrophenanthraquinone (CHRISTIE and KENNER), 473.

$C_{14}H_6O_5S$ Thionylhystazarin (GREEN), 2201.

$C_{14}H_6O_6S$ 2:3-Thionylanthragallol (GREEN), 2202.
Thionylpurpurin (GREEN), 2200.

$C_{14}H_6O_{10}N_4$ 3:5:3′:5′-Tetranitrobenzil (CHRISTIE and KENNER), 475.

$C_{14}H_7O_4Cl$ Chlorohydroxyanthraquinones (GREEN), 1431, 1435, 2203.

$C_{14}H_7O_{16}N_3$ 4:6:4′-Trinitrodiphenic acids, and their quinine salts (CHRISTIE and KENNER), 473.

$C_{14}H_8OCl_2$ 4:10-Dichloroanthrone (MATTHEWS), 243.

$C_{14}H_8OS_4$ 3-Keto-1:4-benzdithian-2:2′-*spiro*-1′:3′-benzdithiole (HURTLEY and SMILES), 2269.

$C_{14}H_8O_4N_2$ 3:4′-Dinitrotolane (HARRISON), 1235.

7-Nitro-4-keto-3-phenyl-1:2-benzoxazine (BISHOP and BRADY), 812.

6-Nitro-3-keto-2-phenyl-ψ-indole (BISHOP and BRADY), 812.

$C_{14}H_8O_4S_5$ 2:2′-Bis-1:3-benzdithiylium sulphate (HURTLEY and SMILES), 2269.

$C_{14}H_8O_5N_2$ Triacetyldiaminoveratrole (OXFORD), 2008.

$C_{14}H_8O_6N_2$ Dinitrobenzils, isomeric (CHATTAWAY and COULSON), 1070.

$C_{14}H_8O_6N_4$ Dinitrodiphenic hydrazides (CHRISTIE, HOLDERNESS, and KENNER), 675.

$C_{14}H_8O_8N_2$ β-Dinitrodiphenic acid, constitution and resolution of, and its salts (CHRISTIE, HOLDERNESS, and KENNER). 671.

2:2′-Dinitrodiphenyl-3:3′-dicarboxylic acid (BURTON, HAMMOND, and KENNER), 1804.

$C_{14}H_8I_4S_4$ Tetraiodobis-1:3-benzdithiolene (HURTLEY and SMILES), 2270.

$C_{14}H_9OCl$ 10-Chloroanthrone (MATTHEWS). 242.

$C_{14}H_9O_2Cl$ Chloro-10-hydroxyanthrones (MATTHEWS), 241.

$C_{14}H_9O_3Cl$ 2-Chloro-3-benzoyloxybenzaldehyde (HODGSON and BEARD), 150.

$C_{14}H_9O_6N_3$ 2:4-Dinitrobenzil monoximes, behaviour of, in the Beckmann change (BISHOP and BRADY), 810.

$C_{14}H_9N_3S_2$ 1-Aminoazothiazole, and its hydrochloride (HUNTER), 1396.

$C_{14}H_{10}O_2N_2$ 6-Nitro-2-methyl-α-naphthaquinoline, and its chloroplatinate (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2254.

$C_{14}H_{10}O_2N_4$ Substance, from reduction of tetranitrodiphenic acid (CHRISTIE and KENNER), 474.

$C_{14}H_{10}O_4N_2$ 3:4′-Dinitrostilbene (HARRISON and WOOD), 580.

$C_{14}H_{10}O_5N_2$ Nitrophenyl nitrobenzyl ketones (HARRISON and WOOD), 581.

$C_{14}H_{10}O_6N_4$ β-Dinitrodiphenamide (CHRISTIE, HOLDERNESS, and KENNER), 674.

$C_{14}H_{10}O_8N_6$ *p*-Acetylaminobenzenediazonium picrate (GRAY), 3180.

$C_{14}H_{10}NCl$ Chloromethylnaphthaquinolines (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2252.

$C_{14}H_{10}NBr$ 6-Bromo-2-methyl-α-naphthaquinoline, and its salts (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2255.

$C_{14}H_{11}ON_3$ 1-Acetyl-5-phenyl-1:2:3-benztriazole (BELL and KENYON), 2709.

4′-Amino-3-phenylphthalaz-4-one, and its hydrochloride (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 703.

$C_{14}H_{11}O_2N$ 4′-Hydroxy-*N*-phenylphthalimidine (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 704.

$C_{14}H_{11}O_2Cl$ Chloro-*m*-tolyl benzoates (GIBSON), 1425.

$C_{14}H_{11}O_3N_3$ 3:5-Dicyano-6-hydroxy-4-benzyl-2-pyridone, and its ammonium salt (LINSTEAD and WILLIAMS), 2747.

Substance, from reduction of trinitrodiphenic acid (CHRISTIE and KENNER), 475.

$C_{14}H_{11}O_4N_3$ *o*-Piperonal *p*-nitrophenylhydrazone (PERKIN and TRIKOJUS), 2932.

$C_{14}H_{11}NI_2$ 3:6-Di-iodo-9-ethylcarbazole (TUCKER), 552.

$C_{14}H_{11}N_2S_2$ 2-Aminotolyl 5-disulphide (CHILD and SMILES), 2700.

$C_{14}H_{12}ON_2$ 4′-Amino-*N*-phenylphthalimidine (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 703.

$C_{14}H_{12}O_4N_2$ Dinitro-4:4′-ditolyl (DENNETT and TURNER), 480.

$C_{14}H_{12}O_4S_4$ 3:7-Dimethoxy-2:6-dihydroxythianthren disulphide (SEN and RÂY), 1140.

$C_{14}H_{12}O_5N_2$ 3:4′-Dinitro-αβ-diphenylethyl alcohol (HARRISON and WOOD), 580.

$C_{14}H_{12}O_6N_2$ Dinitrobenzyloxyanisoles (OXFORD and ROBINSON), 386; (ROBINSON and SMITH), 399.

$C_{14}H_{13}ON$ γ-Oximinobutenylnaphthalenes (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2258.

$C_{14}H_{13}O_2N$ Acetoaceto-α-naphthalide (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2253.

Nitro-4:4′-ditolyl (DENNETT and TURNER), 480.

$C_{14}H_{13}O_4N$ Nitrobenzyloxyanisoles (ALLAN and ROBINSON), 382; (OXFORD and ROBINSON), 386; (ROBINSON and SMITH), 400.

$C_{14}H_{13}O_4N_3$ 2:4-Dinitro-3-benzylaminotoluene (GORNALL and ROBINSON), 1984.

Dinitro-4-dimethylaminodiphenyls (BELL and KENYON), 2711.

$C_{14}H_{14}ON_2$ 3-Amino-4-acetylaminodiphenyl (BELL and KENYON), 2708.

4-Aminophenyl 3-aminobenzyl ketone (HARRISON), 1238.

$C_{14}H_{14}O_2N_2$ 2′-Nitro-4-dimethylaminodiphenyl (BELL and KENYON), 2707.

$C_{14}H_{14}O_2Te$ Bis-*p*-anisyl telluride (MORGAN and KELLETT), 1085.

$C_{14}H_{14}O_2Te_2$ Bis-*p*-anisylditelluride (MORGAN and KELLETT), 1084.

$C_{14}H_{14}O_3N_2$ *p*-Azoxybenzyl alcohol (SHOESMITH and TAYLOR), 2834.

$C_{14}H_{14}NBr$ Bromo-4-dimethylaminodiphenyl (KENYON and ROBINSON), 3052.

$C_{14}H_{14}N_2S$ 2-*n*-Propylamino-β-naphthathiazole (DYSON, HUNTER, and SOYKA), 2967.

$C_{14}H_{15}ON$ γ-Ketobutylnaphthalene oximes (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2258.

$C_{14}H_{15}O_2N$ Methyl tetrahydrocarbazolecarboxylates (COLLAR and PLANT), 809.

$C_{14}H_{16}N_2S$ *s*-α-Naphthyl-*n*-propylthiocarbamide (DYSON, HUNTER, and SOYKA), 2967.

$C_{14}H_{17}ON$ α-Δ^1-*cyclo*Hexenylacetophenone oxime (FARROW and KON), 2133.

$C_{14}H_{17}ON_3$ α-Δ^1-*cyclo*Pentenylacetophenone semicarbazone (FARROW and KON), 2136.

$C_{14}H_{17}O_2N$ 6:7-Dimethoxytetrahydrocarbazole (PERKIN and RUBENSTEIN), 360.

$C_{14}H_{17}O_6N$ Ethyl β-hydroxy-β-(2-carboxydimethoxyphenyl)ethylcarbamate lactones (EDWARDS), 746.

$C_{14}H_{18}O_4Hg$ 2-Hydroxy-3-acetoxymercuri-5-*iso*amylbenzaldehyde (HENRY and SHARP), 2438.

$C_{14}H_{18}O_5Hg_2$ 2:6-Diacetoxymercuri-*p*-*tert*.-butylphenol (HENRY and SHARP), 2434.

Diacetoxymercuricarvacrol (HENRY and SHARP), 2436.

$C_{14}H_{19}ON_3$ α-Phenyl-γ-ethylpenten-α-one semicarbazones (FARROW and KON), 2137.

$C_{14}H_{20}ON_4$ 1-Methyl*cyclo*hexan-2-one δ-anilinosemicarbazone (BAIRD and WILSON), 2372.

$C_{14}H_{20}N_2S$ 1-*n*-Heptylaminobenzthiazole (HUNTER), 2957.

$C_{14}H_{21}ON$ *cyclo*Hexenyl*cyclo*hexanone imide (KON and NUTLAND), 3106.

$C_{14}H_{21}O_4N$ *p*-Dimethylbenzylidenepentaerythritol (FAIRBOURNE and WOODLEY), 3240.

$C_{14}H_{22}ON_4$ Dipropyl ketone δ-anilinosemicarbazones (BAIRD and WILSON), 2372.

$C_{14}H_{22}N_2S$ *s*-Phenyl-*n*-heptylthiocarbamide (HUNTER), 2957.

$C_{14}H_{23}ON_3$ 2-Methyl-2-Δ^1-*cyclo*hexenyl*cyclo*hexanone semicarbazone (KON and NUTLAND), 3105.

$C_{14}H_{25}ON_3$ Butyl-Δ^1-*cyclo*hexenylacetone semicarbazone (KON and SMITH), 1797.

14 IV

$C_{14}H_5O_7ClS_2$ 1:2-Thionyl-7-chlorothionylanthrapurpurin (GREEN), 2200.

$C_{14}H_6O_6N_2Cl_2$ β-Dinitrodiphenic chloride (CHRISTIE, HOLDERNESS, and KENNER), 673.

$C_{14}H_8OClBr$ 1-Chloro-10-bromoanthrone (MATTHEWS), 241.

$C_{14}H_9ONI_2$ Di-iodo-9-acetylcarbazole (TUCKER), 548.

$C_{14}H_9O_4N_2Cl$ α-Chlorodinitrostilbenes (HARRISON and WOOD), 581.

$C_{14}H_9O_5N_2Br_3$ 3:5-Dibromodinitro-4-acetylaminodiphenyl (KENYON and ROBINSON), 3053.

$C_{14}H_{10}ONCl_3$ 3:5:4′-Trichloro-4-acetylaminodiphenyl (SCARBOROUGH and WATERS), 560.

$C_{14}H_{10}ONBr_3$ 3:5:4′-Tribromo-4-acetylaminodiphenyl (SCARBOROUGH and WATERS), 562.

$C_{14}H_{10}O_3N_2Cl_2$ Benzoyl-2:6-dichloro-4-nitroaceto-*m*-toluidide (DAVIES and LEEPER), 1417.

$C_{14}H_{10}O_3N_2Br_2$ Dibromo-4′-nitro-4-acetylaminodiphenyl (KENYON and ROBINSON), 3053.

$C_{14}H_{10}O_4N_2Cl_2$ 3:4-Dinitrostilbene dichloride (HARRISON and WOOD), 581.

$C_{14}H_{10}O_4N_2Br_2$ 3:4′-Dinitrostilbene dibromide (HARRISON), 1234.

$C_{14}H_{11}ONCl_2$ Dichloro-4-acetylaminodiphenyls (KENYON and ROBINSON), 3053.

$C_{14}H_{11}ONBr_2$ Dibromo-4-acetylaminodiphenyls (SCARBOROUGH and WATERS), 561; (KENYON and ROBINSON), 3052.

$C_{14}H_{11}ONS$ 2-Keto-1-*o*-tolyl-1:2-dihydrobenz*iso*thiazole (MCCLELLAND and GAIT), 923.

$C_{14}H_{11}O_3N_2Br$ 4-Bromo-3′-nitro-4′-acetylaminodiphenyl (LE FÈVRE and TURNER), 2045.

$C_{14}H_{11}O_3N_3Cl_2$ Dichloro-3-methoxybenzaldehyde *o*-nitrophenylhydrazones (HODGSON and BEARD), 155.

$C_{14}H_{12}ONCl$ Chloro-4-acetylaminodiphenyls (SCARBOROUGH and WATERS), 559.

Diphenylyl-4-acetylchloroamine (BELL, KENYON, and ROBINSON), 1246.

$C_{14}H_{12}ONBr$ 3-Bromo-4-acetylaminodiphenyl (KENYON and ROBINSON), 3051.

$C_{14}H_{12}ONI$ 1-Phenylbenzoxazole methiodide (CLARK), 235.

$C_{14}H_{12}ON_2Br_2$ *o*-Azoxybenzyl bromide (SHOESMITH and TAYLOR), 2832.

$C_{14}H_{12}O_3N_3Cl$ Chloro-3-methoxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and BEARD), 154.

$C_{14}H_{12}O_4N_2Hg$ 4-Mercuribis-2-nitrotoluene (COFFEY), 640.

$C_{14}H_{12}O_6N_2S_2$ 2:2′- and 4:4′-Dinitro-5:5′-dimethoxydiphenyl disulphides (HODGSON and HANDLEY), 543.

$C_{14}H_{13}O_5NS$ *N*-4-Toluenesulphonyl-3-amino-4-hydroxybenzoic acid (HEWITT, KING, and MURCH), 1368.

$C_{14}H_{13}O_8N_2As$ Nitroanisoylaminohydroxyphenylarsinic acids, and their salts (HEWITT and KING), 826.

$C_{14}H_{13}NClAs$ 10-Chloro-2:8-dimethyl-5:10-dihydrophenarsazine (BURTON and GIBSON), 468.

$C_{14}H_{14}OIAs$ 10:10-Dimethylphenoxarsonium iodide (ROBERTS and TURNER), 1209.

$C_{14}H_{14}O_2NAs$ 2:8-Dimethylphenarsazinic acid, and its salts (BURTON and GIBSON), 469.

$C_{14}H_{14}O_2Cl_2Te$ Di-*p*-anisyltelluridichloride (MORGAN and KELLETT), 1085.

$C_{14}H_{14}O_4N_2S$ Benzoyl-*m*-tolylenediamine-3-sulphonic acid (GORNALL and ROBINSON), 1983.

$C_{11}H_{14}O_6N_4S$ 2-Nitrotolyl 2-nitrotoluene-5-sulphazide (COFFEY), 642.

$C_{14}H_{14}N_2Br_6S$ 2-*n*-Propylamino-β-naphthathiazole hexabromide (DYSON, HUNTER, and SOYKA), 2967.

$C_{14}H_{15}O_3NS$ *N*-*p*-Toluenesulphonylmethylaminophenols (HEWITT, KING, and MURCH), 1368.

$C_{14}H_{15}O_6N_2AS$ Aminoanisoylaminohydroxyphenylarsinic acids, and their salts (HEWITT and KING), 826.

$C_{14}H_{16}O_5NAs$ *N*-Acetyldiphenylamine-*p*-arsinic acid (BURTON and GIBSON), 460.

$C_{14}H_{17}ON_3S$ 2:4-Diketo-3-phenyl-5-ethyltetrahydrothiazole-2-*iso*propylidenehydrazone (STEPHEN and WILSON), 2534.

$C_{14}H_{19}N_2BrS$ 5-Bromo-1-*n*-heptylaminobenzthiazole (HUNTER and SOYKA), 2964.

$C_{14}H_{19}N_2Br_3S$ 5-Bromo-1-*n*-heptylaminobenzthiazole dibromide (HUNTER and SOYKA), 2964.

$C_{14}H_{21}N_2BrS$ *s*-*p*-Bromophenyl-*n*-heptylthiocarbamide (HUNTER and SOYKA), 2964.

$C_{14}H_{21}N_2Br_3S$ 1-*n*-Heptylaminobenzthiazole dibromide hydrobromide (HUNTER), 2957.

$C_{14}H_{32}ON_{14}Cu_6$ Ethylenediammonium tricuprocyanide hemihydrate (MORGAN and BURSTALL), 2025.

$C_{14}H_{26}O_2N_4Ni$ Ethylenediammino-nickel ethylenediaminobisacetylacetone (MORGAN and SMITH), 920.

$C_{14}H_{22}O_2N_4Cu$ Cupric ethylenediaminobisacetylacetone ethylenediamine hydrate (MORGAN and SMITH), 918.

14 V

$C_{14}H_9ON_2BrS$ 5-Bromo-1-benzoylaminobenzthiazole (HUNTER), 1396.

$C_{14}H_{10}ON_2Br_4S$ 1-Benzoylaminobenzthiazole tetrabromide (HUNTER), 1396.

$C_{14}H_{12}ONCl_2As$ *N*-Acetyldiphenylamine-*p*-arsenious chloride (BURTON and GIBSON), 461.

$C_{14}H_{12}ON_2ClBr$ Chloro-3-methoxybenzaldehyde *p*-bromophenylhydrazones (HODGSON and BEARD), 154.

$C_{14}H_{12}O_3NClS_2$ *p*-Acetylaminophenyl *p*-chlorobenzenethiolsulphonate (CHILD and SMILES), 2702.

$C_{14}H_{15}O_5NBrAs$ 2-Bromo-6′-dimethylaminodiphenylarsinic acid (BURTON and GIBSON), 458.

$C_{14}H_{15}O_7N_2SAs$ 3′-Nitro-4′-toluenesulphonyl-4-methylaminophenylarsinic acid (HEWITT, KING, and MURCH), 1361.

$C_{14}H_{16}O_5NSAs$ 4′-Toluenesulphonyl-4-methylaminophenylarsinic acid (HEWITT, KING, and MURCH), 1360.

$C_{14}H_{17}O_5N_2SAs$ 3′-Amino-4′-toluenesulphonyl-4-methylaminophenylarsinic acid, and its salts (HEWITT, KING, and MURCH), 1363.

$C_{14}H_{20}O_2N_2Cl_6Pd$ Dichloroformo-palladous ethylenediaminobisacetylacetone (MORGAN and SMITH), 921.

C_{15} Group.

$C_{15}H_{24}$ Cadinene, chemistry of (HENDERSON and ROBERTSON), 2811.

Cadinene, β-Caryophyllene, and Cedrene, action of chromyl chloride on (GIBSON, ROBERTSON, and SWORD), 165.

Copaene, new source of (HENDERSON, M'NAB, and ROBERTSON), 3077.

15 II

$C_{15}H_{10}O_3$ Fisetin, synthesis of (ALLAN and ROBINSON), 2334.

$C_{15}H_{10}O_4$ Chrysin, synthesis of (ROBINSON and VENKATARAMAN), 2348.

Quercetin, synthesis of (ALLAN and ROBINSON), 2334.

$C_{15}H_{10}O_5$ Galangin, synthesis of (HEAP and ROBINSON), 2337.

Prunetol, constitution of, and its identity with genistein (BAKER and ROBINSON), 2713.

$C_{15}H_{12}O_5$ ω-Benzoyloxyresacetophenone (HEAP and ROBINSON), 2338.
$C_{15}H_{12}O_6$ ω-Benzoyloxyphloracetophenone (HEAP and ROBINSON), 2340.
$C_{15}H_{14}O$ *d*-Methyldeoxybenzoin (MCKENZIE, ROGER, and WILLS), 787.
$C_{15}H_{14}O_3$ Benzoyl*iso*creosol (GRAESSER-THOMAS, GULLAND, and ROBINSON), 1973.
3:4′-Dimethoxybenzophenone (LEA and ROBINSON), 2355.
$C_{15}H_{14}O_5$ 2:4:6-Trihydroxyphenyl *p*-methoxybenzyl ketone (+ H_2O) (BAKER and ROBINSON), 2717.
$C_{15}H_{16}O_3$ 2-Methoxybenzyloxyanisoles (OXFORD and ROBINSON), 389.
$C_{15}H_{16}O_6$ 3:4:5-Triacetoxy-ω-methoxyacetophenone (GATEWOOD and ROBINSON), 1965.
$C_{15}H_{16}N_6$ 3-Propyl-1:2:4-triazole-5-azo-β-naphthylamines (REILLY and DRUMM), 1736.
$C_{15}H_{18}O_4$ 3-Carbethoxybenzylacetylacetones, and their copper salts (MORGAN and PORTER), 1258.
3-*m*-Carboxybenzylbutyrylacetone, and its salts (MORGAN and PORTER), 1260.
$C_{15}H_{20}O_2$ Substance, from oxidation of β-caryophyllene (GIBSON, ROBERTSON, and SWORD), 165.
$C_{15}H_{22}O_4$ Ethyl 1-*cyclo*hexyl-3:5-diketo*cyclo*hexane-6-carboxylate (KON and SMITH), 1799.
$C_{15}H_{24}O$ Substance, from oxidation of cedrene (GIBSON, ROBERTSON, and SWORD), 166.
$C_{15}H_{24}O_2$ Substance, from oxidation of cadinene (GIBSON, ROBERTSON, and SWORD), 166.
$C_{15}H_{26}O$ Caryophyllene alcohol (HENDERSON, ROBERTSON, and KERR), 66.
Cubebol (HENDERSON and ROBERTSON), 2815.
$C_{15}H_{26}O_4$ Ethyl *cyclo*hexane-1-acetate-1-propionate (NORRIS), 250.
$C_{15}H_{28}O_2$ Caryophyllene glycol (HENDERSON, ROBERTSON, and KERR), 68.
$C_{15}H_{28}O_6$ Ethyl dimethoxyazelate (GOSS and INGOLD), 1476.

15 III

$C_{15}H_{10}O_6N_2$ 3:4′-Dinitro-α-phenylcinnamic acids, stereoisomeric (HARRISON and WOOD), 1198.
$C_{15}H_{11}O_2Cl$ ω-Chlorobenzoylacetophenones (BRADLEY and ROBINSON), 2363.
$C_{15}H_{11}O_3Cl$ Dihydroxyflavylium chlorides (ROBERTSON and ROBINSON), 1953.
$C_{15}H_{11}O_4Cl$ Benzoylvanilloyl chloride (HEAP and ROBINSON), 2342.
Trihydroxyflavylium chlorides (ROBERTSON and ROBINSON), 1954.
$C_{15}H_{11}O_5N_3$ 3:4′-Dinitro-β-hydroxy-α-phenyldihydrocinnamonitrile (HARRISON and WOOD), 1197.
3:4′-Dinitro-α-phenylcinnamamides, stereoisomeric (HARRISON and WOOD), 1197.
$C_{15}H_{11}O_5Cl$ Pelargonidin chloride (+ H_2O) (NOLAN, PRATT, and ROBINSON), 1969.
Tetrahydroxyflavylium chlorides (ROBERTSON and ROBINSON), 1957.
$C_{15}H_{13}ON$ 3-Methoxy-2-phenylindole (ROBINSON and THORNLEY), 3144.
$C_{15}H_{13}O_2N$ 4′-Hydroxy-*N*-phenylphthalimidine methyl ether (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 705.
$C_{15}H_{14}NI$ 3-Iodo-9-*iso*propylcarbazole (TUCKER), 553.
$C_{15}H_{15}ON_5$ 3-*iso*Propyl-1:2:4-triazole-5-azo-β-naphthol (REILLY and DRUMM), 1736.
$C_{15}H_{15}O_2N$ *o*-Benzoylmethylaminoanisole (CLARK), 235.
Methyltetrahydroacridinecarboxylic acid (PERKIN and SEDGWICK), 444.
$C_{15}H_{15}O_3N$ Nitro-2-methoxybenzyloxyanisoles (OXFORD and ROBINSON), 390.
$C_{15}H_{16}O_3N_2$ 5-Nitro-9-acetyl-6-methyltetrahydrocarbazole (MANJUNATH and PLANT), 2261.

$C_{15}H_{16}N_2S$ 2-Butylamino-β-naphthathiazoles (DYSON, HUNTER, and SOYKA), 2967.

$C_{15}H_{17}ON$ 9-Acetyl-6-methyltetrahydrocarbazole (MANJUNATH and PLANT), 2261.

β-Amino-αα-diphenyl-*n*-propyl alcohols (MCKENZIE, ROGER, and WILLS), 786.

$C_{15}H_{17}ON_3$ 2-γ-Ketobutylnaphthalene semicarbazone (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2258.

$C_{15}H_{17}O_2N$ Acetoxy-6-methyltetrahydrocarbazolenines (MANJUNATH and PLANT), 2262.

6-Acetyl-9-methyl-ψ-indoxyl*spirocyclo*pentane (MANJUNATH and PLANT), 2263.

Ethyl tetrahydrocarbazolecarboxylates (COLLAR and PLANT), 809.

$C_{15}H_{19}N_3S$ *s*-α-Naphthylbutylthiocarbamides (DYSON, HUNTER, and SOYKA), 2967.

$C_{15}H_{19}ON_3$ α-Δ^1-*cyclo*Hexenylacetophenone semicarbazone (FARROW and KON), 2132.

$C_{15}H_{19}O_2N$ Cyanolactone of *cyclo*hexenyl*cyclo*hexanone (KON and NUTLAND), 3106.

$C_{15}H_{19}O_3N$ 9-Acetyl-10:11-dihydroxy-6-methylhexahydrocarbazole (MANJUNATH and PLANT), 2262.

$C_{15}H_{20}O_5Hg_2$ 2:6-Diacetoxymercuri-*p*-*iso*amylphenol (HENRY and SHARP), 2435.

$C_{15}H_{21}O_3N$ Cyano-ester of 2-*cyclo*pentylidene*cyclo*pentanone (KON and NUTLAND), 3107.

$C_{15}H_{21}O_4N$ β-Octyl nitrobenzoates (RULE and NUMBERS), 2121.

$C_{15}H_{23}O_2N$ Acetyl-*o*-benzylideneaminophenol, and its hydrolysis (BELL and KENYON), 1893.

$C_{15}H_{24}OCl_2$ Caryophyllene dichlorohydrin anhydride (HENDERSON, ROBERTSON, and KERR), 69.

$C_{15}H_{26}OBr_2$ Cubebol dibromide (HENDERSON and ROBERTSON), 2816.

15 IV

$C_{15}H_{15}ONS$ *dl*-4′-Acetylamino-4-methyldiphenyl sulphoxide, and its resolution (HARRISON, KENYON, and PHILLIPS), 2087.

$C_{15}H_{15}O_2NS$ 4′-Acetylamino-4-methyldiphenyl sulphone (HARRISON, KENYON, and PHILLIPS), 2087.

$C_{15}H_{15}O_2NS_2$ *p*-Tolyl *p*-acetylaminobenzenethiolsulphonate (CHILD and SMILES), 2702.

$C_{15}H_{16}N_2Br_4S$ 2-*n*-Butylamino-β-naphthathiazole tetrabromide (DYSON, HUNTER, and SOYKA), 2967.

$C_{15}H_{17}N_2Br_7S$ 2-*iso*Butylamino-β-naphthathiazole hexabromide hydrobromide (DYSON, HUNTER, and SOYKA), 2968.

$C_{15}H_{24}O_4NI$ *p*-Dimethylbenzylidene pentaerythritol methiodide (FAIRBOURNE and WOODLEY), 3241.

15 V

$C_{15}H_{13}ONClAs$ 10-Chloro-5-acetyl-2-methyl-5:10-dihydrophenarsazine (BURTON and GIBSON), 468.

C_{16} Group.

$C_{16}H_{10}O_6$ 3-Acetylanthragallol (GREEN), 2203.

2-Acetylanthrapurpurin (GREEN), 2201.

$C_{16}H_{12}O_4$ 10-Ethoxy-1-hydroxy-4:9-anthraquinone (GREEN), 1434.

7-Hydroxy-4′-methoxyflavone (ROBINSON and VENKATARAMAN), 2346.

ω-Piperonoylacetophenone (BRADLEY and ROBINSON), 2363.

$C_{16}H_{12}O_5$ Acacetin, synthesis of (ROBINSON and VENKATARAMAN), 2344.

3:7-Dihydroxy-4′-methoxyflavone (HEAP and ROBINSON), 2339.

2-Methylgenistein (BAKER and ROBINSON), 2716.

$C_{16}H_{12}O_6$ Kaempferide, synthesis of, and its salts (HEAP and ROBINSON), 2336.
$C_{16}H_{12}O_7$ *iso*Rhamnetin, synthesis of (HEAP and ROBINSON), 2336.
$C_{16}H_{13}N$ 2-Methylacenaphthpyridine, and its salts (NAIR and SIMONSEN), 3141.
$C_{16}H_{14}O_2$ 2-Hydroxystyryl benzyl ketone (DICKINSON), 2237.
$C_{16}H_{14}O_3$ ω-Methoxybenzoylacetophenones (BRADLEY and ROBINSON), 2359.
$C_{16}H_{16}O_4$ 3:4:3′-Trimethoxybenzophenone (LEA and ROBINSON), 2355.
$C_{16}H_{16}S_2$ 1:4:5:8-Tetramethylthianthren (SEN and RÂY), 1140.
$C_{16}H_{17}N$ Methyl-1:2:3:4-tetrahydroacenaphthpyridines, and their salts (NAIR and SIMONSEN), 3141.
$C_{16}H_{18}O_4$ *m*-Methoxyphenol ethylene ether (PERKIN, RÂY, and ROBINSON), 946.
$C_{16}H_{20}N_2$ 3:3′-Tetramethyldiaminodiphenyl (DUTT), 1181.
$C_{16}H_{24}O_2$ *l*-β-Octyl anisate (RULE and NUMBERS), 2121.
β-Octyl methoxybenzoates (RULE and NUMBERS), 2121.
$C_{16}H_{32}O_4$ 9:10-Dihydroxypalmitic acid (HILDITCH), 1836.

16 III

$C_{16}H_9O_4Cl$ 1-Chloro-4-acetoxyanthraquinone (GREEN), 1434.
5-Chloro-1-acetoxyanthraquinone (GREEN), 2203.
$C_{16}H_{11}O_3N_3$ Quinoxaline derivative of 3-thiol-2-quinolone-4-carboxylic acid (AESCHLIMANN), 2909.
$C_{16}H_{11}O_2Cl$ Chloro-9-anthranyl acetates (MATTHEWS), 241.
$C_{16}H_{11}O_3N$ 1-Phenylacetylisatin (AESCHLIMANN), 2909.
$C_{16}H_{11}O_5N_3$ *N*-4′-Nitrophenyliminoisocarbostyril-3-carboxylic acid (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 705.
$C_{16}H_{12}NCl$ 2-Chloro-4-methylacenaphthpyridine (NAIR and SIMONSEN), 3143.
$C_{16}H_{13}ON$ Hydroxymethylacenaphthpyridines (NAIR and SIMONSEN), 3142.
$C_{16}H_{13}O_3N_3$ 4′-Acetylamino-3-phenylphthalaz-4-one (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 703.
$C_{16}H_{13}O_6Cl$ 7:4′-Dihydroxy-3-methoxyflavylium chloride (+ H_2O) (ROBERTSON and ROBINSON), 1716.
$C_{16}H_{13}O_5N_3$ 1-Hydroxy-3-(4′-nitrophenyl)-1:3-dihydrophthalazine-4-acetic acid (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 700.
$C_{16}H_{13}O_7Cl$ 3:7:3′:4′-Tetrahydroxy-5-methylflavylium chloride (ROBERTSON and ROBINSON), 1955.
$C_{16}H_{13}O_5Br$ 6′-Bromohomopiperonylresacetophenone (BAKER), 1076.
$C_{16}H_{13}O_6N_3$ *o*-Carboxy-α-hydroxycinnamic acid *p*-nitrophenylhydrazide (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 705.
$C_{16}H_{13}O_6Cl$ Morinidin chloride 3-methyl ether (GATEWOOD and ROBINSON), 1962.
Peonidin chloride (NOLAN, PRATT, and ROBINSON), 1968.
Tetrahydroxymethoxyflavylium chloride (+ H_2O) (GATEWOOD and ROBINSON), 1964.
$C_{16}H_{13}O_7Cl$ 5:7:3′:4′:5′-Pentahydroxy-3-methoxyflavylium chloride (+ $2H_2O$) (GATEWOOD and ROBINSON), 1966.
$C_{16}H_{13}O_8N_3$ Dinitrodihomopiperonylamine (PERKIN, RÂY, and ROBINSON), 948.
$C_{16}H_{14}OS_2$ 2-Benzoyl-2-phenyl-1:3-dithiolan (HURTLEY and SMILES), 2267.
$C_{16}H_{14}O_2N$ β-Phenylethylphthalimide (ING and MANSKE), 2350.
$C_{16}H_{14}O_3N_2$ 4′-Acetylamino-*N*-phenylphthalimidine (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 704.
$C_{16}H_{14}O_2Te$ Phenoxtellurine 10:10-diacetate (DREW), 3069.
$C_{16}H_{14}O_8N_4$ 2:3′-Dinitrodiacetylbenzidine (LE FÈVRE and TURNER), 1762.
$C_{16}H_{15}O_2N$ 5-Acetoacetamidoacenaphthene (NAIR and SIMONSEN), 3143.
4′-Hydroxy-*N*-phenylphthalimidine ethyl ether (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 705.

$C_{16}H_{15}O_3N$ Diacetyl-4-hydroxyaminodiphenyl (Bell, Kenyon, and Robinson), 1244.

$C_{16}H_{15}O_4N$ Benzoylphenylserines (Forster and Rao), 1948.

$C_{16}H_{16}O_2N_2$ 3:4-Diacetyldiaminodiphenyl (Bell and Kenyon), 2708.

$C_{16}H_{16}O_4N_2$ 2-Nitro-4-amino-3′:4′-dimethoxystilbene, and its hydrochloride (Ashley), 2805.

$C_{16}H_{16}O_4S_2$ 1:4:5:8-Tetramethylthianthren disulphone (Sen and Rây), 1140.

$C_{16}H_{17}ON$ Benzoyl-β-*p*-tolylethylamine (Titley), 519.

$C_{16}H_{17}O_3N_3$ 1-Hydroxy-3-(4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid (Rowe, Levin, Burns, Davies, and Tepper), 702.

$C_{16}H_{18}ON_2$ 3-Acetylamino-4-dimethylaminodiphenyl (Bell and Kenyon), 2710.

$C_{16}H_{18}ON_4$ Acetone δ-diphenylaminosemicarbazone (Baird and Wilson), 2374.

Acetophenone δ-methylanilinosemicarbazone (Baird and Wilson), 2373.

Methyl benzyl ketone δ-anilinosemicarbazone (Baird and Wilson), 2372.

$C_{16}H_{18}O_2Te_2$ Bis-2-methoxy-*m*-tolyl ditelluride (Morgan and Kellett), 1086.

$C_{16}H_{18}O_4N_4$ Dinitrotetramethylbenzidines (Bell and Kenyon), 2711.

$C_{16}H_{18}N_2S$ 2-Amylamino-β-naphthathiazoles (Dyson, Hunter, and Soyka), 2968.

$C_{16}H_{19}O_5N$ Ethyl 2-carbethoxy-7-methoxyindole-3-acetate (Perkin and Rubenstein), 362.

Protopine, synthesis of (Haworth and Perkin), 1769.

$C_{16}H_{20}N_2S$ *s*-α-Naphthylamylthiocarbamides (Dyson, Hunter, and Soyka), 2968.

$C_{16}H_{20}IAs$ Phenyl-β-phenylethylmethylarsine methiodide (Roberts, Turner, and Bury), 1446.

$C_{16}H_{21}ON_3$ Ethyl-α-Δ^1-*cyclo*pentenylacetophenone (Farrow and Kon), 2136.

Methyl-α-*cyclo*hexenylacetophenone semicarbazone (Farrow and Kon), 2134.

Semicarbazone, from condensation of propiophenone and acetone (Johnson and Kon), 2759.

$C_{16}H_{23}O_3N$ Diacetyl derivative of base $C_{12}H_{19}ON$ (Banfield and Kenyon), 1628.

$C_{16}H_{23}O_3N$ *d*-Methylenecamphor-*l*-alanine ethyl ester (Kipping and Pope), 496.

$C_{16}H_{26}O_6N_2$ Tetramethyl gluconolactone phenylhydrazides (Charlton, Haworth, and Peat), 99.

$C_{16}H_{27}ON_3$ Semicarbazone, from oxidation product of β-caryophyllene (Gibson, Robertson, and Sword), 165.

Semicarbazone, from oxidation product of cedrene (Gibson, Robertson, and Sword), 166.

16 IV

$C_{16}H_{10}O_3NI$ 6-Iodo-3-phenyl-2-quinoline-4-carboxylic acid (Aeschlimann), 2911.

$C_{16}H_{11}O_4NS$ Benzenesulphonyl-1-nitroso-β-naphthol (Edwards), 815.

$C_{16}H_{11}O_6N_2Br_3$ 3:5-Dibromodinitro-4-diacetylaminodiphenyl (Kenyon and Robinson), 3053.

$C_{16}H_{11}O_6N_2S$ 4′-Nitrobenzene-1-azo-β-naphthaquinone-1-sulphonic acid, sodium salt (Rowe, Levin, Burns, Davies, and Tepper), 699.

$C_{16}H_{11}NClAs$ 12-Chloro-7:12-dihydrophenarsazine (Burton and Gibson), 2243.

$C_{16}H_{13}O_4N_2Br$ Dibromo-4′-nitro-4-diacetylaminodiphenyl (Kenyon and Robinson), 3053.

$C_{16}H_{13}ONS$ 5-*p*-Tolylthiol-6-hydroxyquinoline (Brooker and Smiles), 1728.

$C_{16}H_{13}O_2NBr_2$ 3:5-Dibromo-4-diacetylaminodiphenyl (Kenyon and Robinson), 3052.

$C_{16}H_{13}O_6N_2Cl$ 4-Chloro-2:6′-dinitro-3′:4′-dimethoxystilbene (Ashley), 2806.

$C_{16}H_{13}O_7N_2S$ 3-(4′-Nitrophenyl)-1:3-dihydrophthalazine-4-acetic acid-1-sulphonic acid, monosodium salt (Rowe, Levin, Burns, Davies, and Tepper), 699.

$C_{16}H_{14}O_4NCl$ 4-Chloro-2-nitro-3′:4′-dimethoxystilbene (ASHLEY), 2806.

$C_{16}H_{15}O_3N_4Br$ 5-Bromo-1:3-diphenylbarbituric acid hydrazide (MACBETH, NUNAN, and TRAILL), 1252.

$C_{16}H_{15}O_4N_4Cl$ 4-Chloro-2:3′-dinitro-4′-piperazinodiphenyl (LE FÈVRE and TURNER), 2048.

$C_{16}H_{15}O_4N_4Br$ 4-Bromo-2:3′-dinitro-4′-piperazinodiphenyl (LE FÈVRE and TURNER), 2048.

$C_{16}H_{15}O_{16}N_2As$ Nitroethylcarbonatobenzoylaminohydroxyphenylarsinic acids (HEWITT and KING), 826.

$C_{16}H_{16}O_2NCl$ 4-Chloro-2-amino-3′:4′-dimethoxystilbene (ASHLEY), 2806.

$C_{16}H_{16}O_3NAs$ *N*-Acetyl-2:8-dimethylphenarsazinic acid (BURTON and GIBSON), 469.

$C_{16}H_{16}O_4N_2S_2$ Acetanilide disulphoxides (CHILD and SMILES), 2699.

$C_{16}H_{16}O_5N_2S$ *p*-Acetylaminophenyl *p*-acetylaminobenzenesulphonate (CHILD and SMILES), 2699.

$C_{16}H_{16}O_6N_2S_2$ Acetanilide *p*-disulphone (CHILD and SMILES), 2699.

Dicarbomethoxyaminodiphenyl *p*-disulphoxide (CHILD and SMILES), 2698.

$C_{16}H_{16}N_4Br_6S_2$ 1-Imino-2-methyl-1:2-dihydrobenzthiazole tribromide (HUNTER), 1393.

$C_{16}H_{18}ONAs$ 10-*n*-Butoxy-5:10-dihydrophenarsazine (BURTON and GIBSON), 464.

$C_{16}H_{18}N_3ClS$ Methylene-blue, fixation of, by dispersoids (FODOR and RIWLIN), 102; fixation of, by yeast phosphoprotein sols (RIWLIN), 2300.

$C_{16}H_{19}N_2Br_5S$ 2-*n*-Amylamino-6-naphthathiazole tetrabromide hydrobromide (DYSON, HUNTER, and SOYKA), 2968.

$C_{16}H_{19}N_2Br_7S$ 2-*iso*Amylamino-β-naphthathiazole hexabromide hydrobromide (DYSON, HUNTER, and SOYKA), 2968.

16 V

$C_{16}H_{14}O_4N_2I_2As_2$ 5:5′-Di-iodo-3:3′-diacetylamino-4:4′-dihydroxyarsenobenzene (MACALLUM), 1646.

$C_{16}H_{15}ONClAs$ 10-Chloro-5-acetyl-2:8-dimethyl-5:10-dihydrophenarsazine (BURTON and GIBSON), 468.

$C_{16}H_{16}O_2N_6Cl_5Sb$ Di-(acetylaminobenzenediazonium chlorides)-antimony trichloride (GRAY), 3177.

C_{17} Group.

$C_{17}H_{12}O_5$ Benzoylfuroin (GREENE), 331.

$C_{17}H_{14}O_4$ 2-Hydroxystyryl 3:4-dimethoxyphenyl ketone (ROBERTSON and ROBINSON), 1952.

$C_{17}H_{14}O_5$ 5:7-Dihydroxy-4′-methoxy-2-methyl*iso*flavone (BAKER and ROBINSON), 2717.

$C_{17}H_{15}N_3$ 2-Phenyl-6-methyl-4-anilinopyrimidine, and its salts (FORSYTH and PYMAN), 2507.

$C_{17}H_{16}O_2$ 2-Methoxystyryl benzyl ketone (DICKINSON), 2238.

α-Phenyl-2-methoxystyryl methyl ketone (DICKINSON), 2238.

$C_{17}H_{16}O_3$ α-Anisoylpropiophenone (BRADLEY and ROBINSON), 2361.

$C_{17}H_{16}O_4$ ω-3-Methoxybenzoyl-4-methoxyacetophenone (BRADLEY and ROBINSON), 2365.

$C_{17}H_{18}O_3$ Piperonylidene*iso*phorone (BAKER), 668.

$C_{17}H_{18}O_5$ 5:6-Dimethoxy-1-hydrindoneresorcinol (PERKIN, RÂY, and ROBINSON), 949.

$C_{17}H_{20}O$ Substance, from α-Δ¹-*cyclo*hexenylacetophenone (FARROW and KON), 2135.

$C_{17}H_{20}O_2$ α-Benzoylcamphor, absorption spectra of (MORTON and ROSNEY), 708.
Salicylidene-*dl*-piperitone (EARL and READ), 2074.
$C_{17}H_{20}N_2$ Benzylacetone *p*-tolylhydrazone (BAIRD and WILSON), 2374.
$C_{17}H_{22}O_4$ 3-*m*-Carbethoxybenzylbutyrylacetone, and its copper salt (MORGAN and PORTER), 1260.
$C_{17}H_{26}O_7$ Ethyl ω-4-carbethoxy-2-keto*cyclo*pentylmethylsuccinate (INGOLD and SHOPPEE), 1917.
$C_{17}H_{26}O_{13}$ Tetracarbethoxy-*l*-arabinose (HAWORTH and MAW), 1753.
Tetracarbethoxy-*l*-xylose (HAWORTH and MAW), 1754.
$C_{17}H_{28}O_2$ Caryophyllene acetate (HENDERSON, ROBERTSON, and KERR), 68.
$C_{17}H_{30}Sn$ Benzylethyldibutylstannane (LAW), 3243.

17 III

$C_{17}H_{13}ON$ α- and β-Naphthanilides (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2255.
$C_{17}H_{13}O_4N_3$ 2:4-Dinitro-*m*-tolyl-α-naphthylamine (GORNALL and ROBINSON), 1984.
$C_{17}H_{14}OS$ 1-*p*-Tolylthiol-2-naphthol (BROOKER and SMILES), 1728.
$C_{17}H_{15}O_5N_3$ Methyl 1-hydroxy-3-(4′-nitrophenyl)-1:3-dihydrophthalazine-4-acetate (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 700.
$C_{17}H_{16}O_2N_2$ Diacetylaminofluorenes (MORGAN and THOMASON), 2695.
$C_{17}H_{16}O_6N_2$ Piperonylidenenitroaminohomoveratrole (GULLAND and ROBINSON), 1980.
$C_{17}H_{16}O_6N_4$ 2′:3:4′-Trinitro-4-piperidinodiphenyl (LE FÈVRE and TURNER), 2044.
$C_{17}H_{17}ON$ β-Phenyl-Δ^{β}-pentenoic anilide (JOHNSON and KON), 2754.
$C_{17}H_{17}O_2N$ Substance, from β-tolylethylamines and piperonal (TITLEY), 517.
$C_{17}H_{17}O_2N_3$ 2-Hydroxystyryl benzyl ketone semicarbazone (DICKINSON), 2237.
$C_{17}H_{17}O_4N$ *cis*-*O*-Methyl-*N*-benzoylphenylserine (FORSTER and RAO), 1948.
$C_{17}H_{18}N_2S$ 1-Xylidinodimethylbenzthiazoles (HUNTER), 1403.
$C_{17}H_{20}ON_2$ 2-Hydroxy-*s*-*tert*.-butylbenzaldehyde phenylhydrazone (HENRY and SHARP), 2437.
$C_{17}H_{20}ON_4$ Benzylacetone δ-anilinosemicarbazone (BAIRD and WILSON), 2373.
$C_{17}H_{20}N_2S$ 2-*n*-Hexylamino-β-naphthathiazole (DYSON, HUNTER, and SOYKA), 2969.
$C_{17}H_{20}BrAs$ *As*-Methyltetrahydroarsindole benzobromide (ROBERTS, TURNER, and BURY), 1444.
$C_{17}H_{21}ON_3$ Semicarbazone of product from α-Δ^1-*cyclo*pentenylacetone and ethyl sodioacetate (FARROW and KON), 2136.
$C_{17}H_{21}O_4N$ 9-Acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole (MANJUNATH and PLANT), 2262.
$C_{17}H_{22}N_2S$ *s*-α-Naphthyl-*n*-hexylthiocarbamide (DYSON, HUNTER, and SOYKA), 2969.
$C_{17}H_{23}ON_3$ Ethyl-α-*cyclo*hexenylacetophenone semicarbazone (FARROW and KON), 2134.
$C_{17}H_{25}ON$ Salicylidene-*dl*-menthylamines (READ, COOK, and SHANNON), 2230.
$C_{17}H_{26}ON_2$ *dl-iso*Menthylphenylcarbamide (READ, COOK, and SHANNON), 2231.
$C_{17}H_{28}O_3Cl_2$ Caryophyllene dichlorohydrin (HENDERSON, ROBERTSON, and KERR), 69.

17 IV

$C_{17}H_8N_2Br_6S$ 1-*m*-Xylidino-3:5-dimethylbenzthiazole hexabromide (HUNTER), 1403.
$C_{17}H_{11}ON_3S$ Benzthiazole-1-azo-β-naphthol (HUNTER), 1396.

$C_{17}H_{13}O_8N_2Cl$ Glycerol α-chlorohydrin di-*p*-nitrobenzoate (FAIRBOURNE and FOSTER), 3150.

$C_{17}H_{13}NClAs$ Chloromethyl-7:12-dihydrobenzophenarsazines (BURTON and GIBSON), 2244.

$C_{17}H_{14}ON_4S$ Dibenzylidene-3-amino-2:4-diketotetrahydrothiazole-2-hydrazone (STEPHEN and WILSON), 2538.

$C_{17}H_{15}O_2N_4I$ Substance, from quinaldine methiodide and *p*-nitrophenylnitrosoamine (HUMPHRIES), 376.

$C_{17}H_{15}O_3Cl_4Fe$ 3′:4′-Dimethoxyflavylium ferrichloride (ROBERTSON and ROBINSON), 1952.

$C_{17}H_{15}O_4Cl_4Fe$ 7:4′-Dihydroxy-3-methoxy-5-methylflavylium ferrichloride (ROBERTSON and ROBINSON), 1719.

7-Hydroxy-3′:4′-dimethoxyflavylium ferrichloride (ROBERTSON and ROBINSON), 1953.

$C_{17}H_{16}O_4N_2Cl$ 4-Chloro-4′-piperidino-2:3′-dinitrodiphenyl (DENNETT and TURNER), 479.

$C_{17}H_{16}O_4N_2Br$ 4-Bromo-4′-piperidino-2:3′-dinitrodiphenyl (DENNETT and TURNER), 479.

$C_{17}H_{17}O_2N_2Br$ 4-Bromo-3′-nitro-4′-piperidinodiphenyl (LE FÈVRE and TURNER), 2046.

$C_{17}H_{17}N_4SNa$ Sodium diacetophenonethiocarbohydrazone (STEPHEN and TURNER), 2537.

$C_{17}H_{18}N_2Br_4S$ 1-Xylidinodimethylbenzthiazole tetrabromides (HUNTER), 1403.

$C_{17}H_{19}N_2Br_7S$ 1-*m*-Xylidino-3:5-dimethylbenzthiazole hexabromide hydrobromide (HUNTER), 1403.

$C_{17}H_{21}N_2Br_5S$ 2-*n*-Hexylamino-β-naphthathiazole tetrabromide hydrobromide (DYSON, HUNTER, and SOYKA), 2969.

C_{18} Group.

$C_{18}H_{28}$ Substance, from reduction of *iso*phorone (BAKER), 670.

18 II

$C_{18}H_{10}N_4$ Phenazineazine (DUTT), 1180.

$C_{18}H_{14}O_5$ 7-Acetoxy-4′-methoxyflavone (ROBINSON and VENKATARAMAN), 2346.

$C_{18}H_{16}O_3$ 2-(2:3-Dimethoxybenzylidene)-1-hydrindone (PERKIN, RÂY, and ROBINSON), 952.

2-Veratrylidene-1-hydrindone (PERKIN, RÂY, and ROBINSON), 951.

$C_{18}H_{16}O_5$ 5-Hydroxy-7:4′-dimethoxy-2-methyl*iso*flavone (BAKER and ROBINSON), 2718.

$C_{18}H_{16}O_6$ 7-Hydroxy-3:3′:4′-trimethoxyflavone (ALLAN and ROBINSON), 2335.

$C_{18}H_{16}O_7$ 5:7-Dihydroxy-3:3′:4′-trimethoxyflavone (ALLAN and ROBINSON), 2336.

$C_{18}H_{17}O_4$ Benzylidene-β-hydroxy-β-(2-carboxy-4:5-dimethoxyphenyl)ethylamine (EDWARDS), 749.

$C_{18}H_{17}N_3$ 4-Phenylimino-2-phenyldimethyldihydropyrimidine (FORSYTH and PYMAN), 2508.

2-Phenyl-6-methyl-4-methylanilinopyrimidine, and its salts (FORSYTH and PYMAN), 2509.

$C_{18}H_{18}O_3$ ω-4-*iso*Propoxybenzoylacetophenone (BRADLEY and ROBINSON), 2362.

$C_{18}H_{18}O_5$ ω-Anisoyl-3:4-dimethoxyacetophenone (BRADLEY and ROBINSON), 2366.

3:4-Dimethoxyphenyl 3:4-methylenedioxy-β-phenyl-α-aminoethyl ketone, and its salts (CAMPBELL, HAWORTH, and PERKIN), 38.

$C_{18}H_{18}O_5$ ω-3-Methoxybenzoyl-3:4-dimethoxyacetophenone (BRADLEY and ROBINSON), 2366.
$C_{18}H_{18}O_7$ Veratric anhydride (ALLAN and ROBINSON), 2334.
$C_{18}H_{20}O_3$ Piperonylidene-*dl*-piperitone (EARL and READ), 2075.
$C_{18}H_{22}O_2$ Anisylidene-*dl*-piperitone (EARL and READ), 2073.
$C_{18}H_{28}O_6$ Ethyl dicarboxy*cyclo*pentenylmalonate (INGOLD, SHOPPEE, and THORPE), 1487.
$C_{18}H_{30}O_2$ Trimethyl*bicyclo*hexyl-5:5′-dione (BAKER), 669.
$C_{18}H_{32}O_2$ Stearolic acid, hydration of (G. M. and R. ROBINSON), 2205.
$C_{18}H_{34}O_2$ Elaidic acid and Oleic acid, oxidation of (HILDITCH), 1828.
Oleic acid, potassium salt, equilibria of potassium chloride, water, and (MCBAIN and ELFORD), 421.
$C_{18}H_{34}O_3$ 9-Ketostearic acid (G. M. and R. ROBINSON), 2207.
$C_{18}H_{36}O_4$ Dihydroxystearic acids, isomerism of (HILDITCH), 1828.

18 III

$C_{18}H_{11}O_5Br$ Piperonylidene-6:7-methylenedioxy-1-hydrindone (HAWORTH, PERKIN, and STEVENS), 1768.
$C_{18}H_{12}O_4N_2$ Phthalbromomethylimide (BALABAN), 572.
$C_{18}H_{14}ON_2$ 2-Hydroxy-5-phenylazobenzene (BELL and KENYON), 3045.
$C_{18}H_{15}O_2N_3$ *N-o*-Nitrophenylbenzidine (TUCKER), 3035.
$C_{18}H_{15}O_6N_2$ 1-Acetoxy-3-(4′-nitrophenyl)-1:3-dihydrophthalazine-4-acetic acid (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 701.
$C_{18}H_{16}O_2N_2$ 3:4′-Diacetylaminotolane (HARRISON), 1237.
$C_{18}H_{16}O_6S_4$ 3:7-Dimethoxy-2:6-diacetoxythianthren disulphide (SEN and RÂY), 1141
$C_{18}H_{16}O_8N_2$ Ethyl β-dinitrodiphenate (CHRISTIE, HOLDERNESS, and KENNER), 673.
Ethyl 2:2′-dinitrodiphenyl-3:3′dicarboxylate (BURTON, HAMMOND, and KENNER), 1804.
$C_{18}H_{16}O_8N_4$ Anhydrohydrastinine-2:4:6-trinitrotoluene, and its hydrochloride (ROBINSON and WEST), 1987.
$C_{18}H_{17}O_6N$ *iso*Nitroso-3:4-dimethoxyphenyl 3:4-methylenedioxy-*p*-phenylethyl ketone (CAMPBELL, HAWORTH, and PERKIN), 38.
$C_{18}H_{17}O_6Cl$ 7-Methoxy-4-phenyl-2:3-dimethylbenzopyrylium perchlorate (HEILBRON and ZAKI), 1904.
$C_{18}H_{18}ON_4$ 5-Cinnamylideneamino-β-*iso*propyl-1:2:4-triazole (REILLY and DRUMM), 1733.
$C_{18}H_{18}O_2N_2$ 3:4′Diacetylaminostilbene (HARRISON), 1236.
$C_{18}H_{18}O_3N_2$ Acetylaminophenyl acetylaminobenzyl ketones (HARRISON), 1238.
$C_{18}H_{18}O_5N_2$ 2-Nitro-4-acetylamino-3′:4′-dimethoxystilbene (ASHLEY), 2805.
$C_{18}H_{18}N_2Cl$ 4-Anilino-2-phenyldimethylpyrimidinium chloride (FORSYTH and PYMAN), 2509.
$C_{18}H_{18}N_3I$ 4-Anilino-2-phenyldimethylpyrimidinium iodide (FORSYTH and PYMAN), 2508.
$C_{18}H_{19}ON$ β-Phenyl-Δβ-hexenoic anilide (JOHNSON and KON), 2755.
β-*iso*Propylcinnamanilide (JOHNSON and KON), 2757.
$C_{18}H_{19}O_2N$ Ethyl β-5-acenaphthylaminocrotonate (NAIR and SIMONSEN), 3142.
$C_{18}H_{19}O_4N_3$ 1-Acetoxy-3-(4′-aminophenyl)tetrahydrophthalazine-4-acetic acid (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 702.
$C_{18}H_{20}O_2N_2$ 3:4′-Diacetylaminodibenzyl (HARRISON), 1236.
$C_{18}H_{20}O_3N_4$ Acetophenone δ-carbethoxyanilinosemicarbazone (BAIRD and WILSON), 2375.

$C_{18}H_{21}O_3N$ Neopine, constitution of, and its hydrobromide (VAN DUIN, ROBINSON, and SMITH), 903.

$C_{18}H_{22}ON_2$ 2-Hydroxy-5-*iso*amylbenzaldehyde phenylhydrazone (HENRY and SHARP), 2438.

$C_{18}H_{22}ON_4$ Benzylacetone δ-methylanilinosemicarbazone (BAIRD and WILSON), 2374.

$C_{18}H_{22}O_2N_2$ Substance and its potassium salt, from β-phenylhydroxylamine and acetone (BANFIELD and KENYON), 1621.

$C_{18}H_{22}N_2S$ 2-*n*-Heptylamino-β-naphthathiazole (DYSON, HUNTER, and SOYKA), 2969.

$C_{18}H_{23}ON_3$ Semicarbazone of substance $C_{17}H_{20}O$ (FARROW and KON), 2135.

$C_{18}H_{23}O_4N$ *cyclo*Hexane*spirocyclo*hexan-3-ol *p*-nitrobenzoate (NORRIS), 250.

$C_{18}H_{23}O_5N$ Cryptopine, synthesis of (HAWORTH and PERKIN), 1769.
Dihydroxydihydrocodeine (CAHN and ROBINSON), 910.

$C_{18}H_{24}N_2S$ *s*-α-Naphthyl-*n*-heptylthiocarbamide (DYSON, HUNTER, and SOYKA), 2969.

$C_{18}H_{26}O_6N_2$ Benzoquinone derivatives of butyl glycines (MORGAN), 80.

$C_{18}H_{29}O_7N_3$ Ethyl ω-4-carbethoxy-2-keto*cyclo*pentylmethylsuccinate semicarbazone (INGOLD and SHOPPEE), 1917.

18 IV

$C_{18}H_{11}O_5N_3Cl$ 4-Chloro-2:3′-dinitro-4′-phenoxydiphenyl (LE FÈVRE and TURNER), 2048.

$C_{18}H_{11}O_5N_3Br$ 4-Bromo-2:3′-dinitro-4′-phenoxydiphenyl (LE FÈVRE and TURNER), 2047.

$C_{18}H_{12}O_4N_3Cl$ 4-Chloro-2:3′-dinitro-4′-anilinodiphenyl (LE FÈVRE and TURNER), 2047.

$C_{18}H_{12}O_4N_3Br$ 4-Bromo-2:3′-dinitro-4′-anilinodiphenyl (LE FÈVRE and TURNER), 2047.

$C_{18}H_{15}O_3Cl_4Fe$ 2:3-Indeno(1:2)dimethoxybenzopyrylium ferrichlorides (PERKIN, RÂY, and ROBINSON), 951.

$C_{18}H_{17}ON_3S$ 2:4-Diketo-3:5-diphenyltetrahydrothiazole-2-*iso*propylidenehydrazone (STEPHEN and WILSON), 2534.

$C_{18}H_{17}O_3N_4I$ Substance, from quinaldine ethiodide and *p*-nitrophenylnitrosoamine (HUMPHRIES), 376.

$C_{18}H_{17}O_3Cl_4Fe$ 7-Methoxy-4-phenyl-2:3-dimethylbenzopyrylium ferrichloride (HEILBRON and ZAKI), 1904.

$C_{18}H_{17}O_4Cl_4Fe$ Trimethoxyflavylium ferrichlorides (ROBERTSON and ROBINSON), 1954.

$C_{18}H_{18}O_3NCl$ 4-Chloro-2-acetylamino-3′:4′-dimethoxystilbene (ASHLEY), 2806.

$C_{18}H_{19}O_2N_4I$ 2-Formyl-6-methylquinoline *p*-nitrophenylhydrazone (HUMPHRIES), 376.

$C_{18}H_{20}O_2N_2S_2$ 2-Acetylaminotolyl 5-disulphide (CHILD and SMILES), 2700.

$C_{18}H_{20}O_4N_2S_2$ 2-Acetylaminotolyl 5-disulphoxide (CHILD and SMILES), 2701.
Dicarbethoxyaminodiphenyl *p*-disulphide (CHILD and SMILES), 2698.

$C_{18}H_{20}O_6N_2S_2$ Dicarbethoxyaminodiphenyl *p*-disulphoxide (CHILD and SMILES), 2698.

$C_{18}H_{20}O_6N_4S$ 6′-Nitromethoxyethoxyphenyl-4:5-thiotriazocatechol methyl ethyl ether (ALLAN and ROBINSON), 379.

$C_{18}H_{22}N_2Br_{14}S$ 2-*n*-Heptylamino-β-naphthathiazole tetradecabromide (DYSON, HUNTER, and SOYKA), 2969.

$C_{18}H_{44}N_{18}S_6Cu_3$ Tetratriaminopropanetricupric hexathiocyanate (MANN), 2685.

18 V

$C_{18}H_{13}ONBr_2S_2$ 2:5-Dibromophenyl 4-acetylaminonaphthyl disulphide (CHILD and SMILES), 2701.

C_{19} Group.

$C_{19}H_{12}O_4$ Δ^1-*cyclo*Hexenylmalonic acid (KON and SPEIGHT), 2733.

$C_{19}H_{15}N$ 4-Benzylideneaminodiphenyl (BELL and KENYON), 2707.

$C_{19}H_{16}O_7$ Diacetyl-ω-benzoyloxyresacetophenone (HEAP and ROBINSON), 2338.

$C_{19}H_{18}O_4$ 2-*m*-Methoxybenzylidene-5:6-dimethoxy-1-hydrindone (PERKIN, RÂY, and ROBINSON), 950.

$C_{19}H_{18}O_5$ Dimethoxydihydroxydistyryl ketones (MCGOOKIN and SINCLAIR), 1579.

5:7:4′-Trimethoxy-2-methyl*iso*flavone (BAKER and ROBINSON), 2718.

$C_{19}H_{18}O_6$ 2-Veratrylidene-4:6-dimethoxycoumaranone (PERKIN, RÂY, and ROBINSON), 951.

$C_{19}H_{20}O_5$ 3:4-Dimethoxystyryl veratryl ketone (PERKIN, RÂY, and ROBINSON), 951.

$C_{19}H_{22}O_4$ 3-Homoveratryl-7-methoxychroman (PERKIN, RÂY, and ROBINSON), 946.

$C_{19}H_{26}O_3$ Menthyl acetophenone-*o*-carboxylate (RULE and SMITH), 556.

$C_{19}H_{36}O_3$ 13-Ketononadecoic acid (G. M. and R. ROBINSON), 2207.

$C_{19}H_{38}O_2$ Propyl palmitate (FEAR and MENZIES), 938.

19 III

$C_{19}H_{13}O_4N$ β-Hydroxy-β-(2-carboxy-3:4-dihydroxyphenyl)ethylamine, and its hydrochloride (EDWARDS), 746.

$C_{19}H_{13}O_5N$ 2:3:9:10-Bismethylenedioxyoxyprotoberberine (HAWORTH and PERKIN), 1780.

$C_{19}H_{15}ON$ 4-Benzylideneamino-4′-hydroxydiphenyl (BELL and KENYON), 2712.

$C_{19}H_{15}O_4N$ 2:3:9:10-Bismethylenedioxydihydroprotoberberine, and its hydrochloride (HAWORTH and PERKIN), 1783.

$C_{19}H_{15}O_5N$ 6:7-Methylenedioxy-3-(3′:4′-dimethoxybenzoyl)*iso*quinoline (CAMPBELL, HAWORTH, and PERKIN), 40.

$C_{19}H_{15}O_6N$ *N*-β-Piperonylethyl-3:4-methylenedioxyhomophthalimide (HAWORTH and PERKIN), 1779.

$C_{19}H_{15}NS$ *N*-Phenylbenziminophenyl thioether (CHAPMAN), 2298.

$C_{19}H_{16}ON_2$ 3-Amino-4-benzoylaminodiphenyl (BELL and KENYON), 2709.

4-Hydroxyaldehydodiphenyl phenylhydrazone (BELL and KENYON), 3047.

$C_{19}H_{16}O_3S$ 4-*p*-Toluenesulphonyloxydiphenyl (BELL and KENYON), 3049.

$C_{19}H_{17}O_4N$ 2:3:9:10-Bismethylenedioxytetrahydroprotoberberine, and its hydrochloride (HAWORTH and PERKIN), 1780.

6:7-Methylenedioxy-3-(3′:4′-dimethoxybenzyl)*iso*quinoline, and its picrate (CAMPBELL, HAWORTH, and PERKIN), 41.

$C_{19}H_{17}O_4P$ *m*-Hydroxytriphenylmethylphosphinic acid, and its sodium salt (BOYD and SMITH), 2330.

$C_{19}H_{17}O_5N$ 6-7-Methylenedioxy-3-(α-hydroxy-3′:4′-dimethoxybenzyl)*iso*quinoline and its picrate (CAMPBELL, HAWORTH, and PERKIN), 40.

$C_{19}H_{17}O_7N$ *N*-β-Piperonylethyl-3:4-methylenedioxyhomophthalamic acid (HAWORTH and PERKIN), 1780.

$C_{19}H_{17}O_7N_3$ Substance, from dehydrogenation of tetra*cyclo*squalene (HARVEY, HEILBRON, and KAMM), 3138.

$C_{19}H_{17}N_3S$ 4′-Aminodiphenylylphenylthiocarbamide (LE FÈVRE and TURNER), 2484.

$C_{19}H_{18}ON_2$ *p*-Hydroxy-*p′p″*-diaminotriphenylmethane (DUTT), 1174.

$C_{19}H_{18}O_3N_2$ Triacetyl-2:7-diaminofluorine (MORGAN and THOMASON), 2695.

$C_{19}H_{19}O_5N$ β-Benzoyloxy-β-(2-carboxy-3:4-dimethoxyphenyl)ethylmethylamine lactone (EDWARDS), 747.

6:7-Methylenedioxy-3-(3′:4′-dimethoxybenzoyl)-1:2:3:4-tetrahydro*iso*quinoline, and its salts (CAMPBELL, HAWORTH, and PERKIN), 39.

$C_{19}H_{20}N_3I$ 4-Methylanilino-2-phenyldimethylpyrimidinium iodide (FORSYTH and PYMAN), 2509.

$C_{19}H_{21}O_4N$ 6:7-Methylenedioxy-3-(3′:4′-dimethoxybenzyl)-1:2:3:4-tetrahydro*iso*quinoline, and its salts (CAMPBELL, HAWORTH, and PERKIN), 41.

$C_{19}H_{23}O_3N$ 1-1′-Hydroxy*cyclo*pentane-1′-carboxylyl-*p*-toluidino*cyclo*pentane-1-carboxylactone (OAKESHOTT and PLANT), 1212.

$C_{19}H_{22}O_8N_2$ Anhydrocotarnine-2:4-diaminotoluene (ROBINSON and WEST), 1985.

$C_{19}H_{23}O_9N_5$ Nitrobenzyltriethylammonium picrates (GOSS, INGOLD, and WILSON), 2450.

$C_{19}H_{24}O_7N_4$ Benzyltriethylammonium picrate (GOSS, INGOLD, and WILSON), 2450.

$C_{19}H_{29}O_2N$ Dihydrodeoxytetrahydro-α-methylmorphimethine (CAHN), 2567.

$C_{19}H_{35}IAs$ Di*cyclo*hexylphenylarsine methiodide (ROBERTS, TURNER, and BURY), 1446.

$C_{19}H_{36}O_2Cl_2$ β-Palmityl dichlorohydrin (WHITBY), 1460.

19 IV

$C_{19}H_{11}ONI_2$ 3:6-Di-iodo-9-benzoylcarbazole (TUCKER), 549.

$C_{19}H_{12}ONI$ 3-Iodo-9-benzoylcarbazole (TUCKER), 549.

$C_{19}H_{14}ONCl$ 10-Hydroxyanthranyl-9-pyridinium chloride ($+H_2O$) (MATTHEWS), 243.

$C_{19}H_{14}OCl_3P$ *p*-Chlorotriphenylmethoxyphosphorus dichloride (BOYD and SMITH), 2327.

$C_{19}H_{14}O_4NCl$ 2:3:9:10-Bismethylenedioxyprotoberberinium chloride (HAWORTH and PERKIN), 1784.

$C_{19}H_{14}O_4N_2Cl$ 4-Chloro-2:3′-dinitro-4′-methylanilinodiphenyl (LE FÈVRE and TURNER), 2047.

$C_{19}H_{14}O_4N_2Br$ 4-Bromo-2:3′-dinitro-4′-methylanilinodiphenyl (LE FÈVRE and TURNER), 2047.

$C_{19}H_{14}O_7N_2S$ 3:4′-Dinitro-4-hydroxydiphenyl *p*-toluenesulphonate (BELL and KENYON), 3049.

$C_{19}H_{15}O_5NS$ 4-*p*-Toluenesulphonyloxy-4′-nitrodiphenyl (BELL and KENYON), 3049.

$C_{19}H_{15}O_5Cl_4Fe$ 2:3[5:6-Dimethoxyindeno(1:2)]-6:7-methylenedioxybenzopyrylium ferrichloride (PERKIN, RÂY, and ROBINSON), 952.

2:3-[7-Methoxychromeno(4:3)]-6:7-dimethoxybenzopyrylium ferrichloride (PERKIN, RÂY, and ROBINSON), 950.

$C_{19}H_{16}ONAs$ 10-Benzyloxy-5:10-dihydrophenarsazine (BURTON and GIBSON), 464.

$C_{19}H_{16}ON_2S$ Phenyl 4′-aminodiphenylylthiocarbamate (LE FÈVRE and TURNER), 2483.

$C_{19}H_{16}O_3ClP$ *p*-Chlorotriphenylmethylphosphinic acid, and its potassium salt (BOYD and SMITH), 2328.

$C_{19}H_{16}O_3BrP$ *p*-Bromotriphenylmethylphosphinic acid, and its salts (BOYD and SMITH), 2328.

$C_{19}H_{16}O_4N_2S$ 3-Nitro-4-*p*-toluenesulphonylaminodiphenyl (BELL and KENYON), 2708.

$C_{19}H_{17}O_3NS$ 4-Aminodiphenyl *p*-toluenesulphonate (BELL, KENYON, and ROBINSON), 1246.

$C_{19}H_{17}O_4Cl_4Fe$ 2:3[5:6-Dimethoxyindeno(1:2)]-8-methoxybenzopyrylium ferrichloride (PERKIN, RÂY, and ROBINSON), 953.

$C_{19}H_{18}ON_4S$ 3-Phenylmethylmethyleneamino-2:4-diketotetrahydrothiazole 2-phenylmethylmethylenehydrazone (STEPHEN and WILSON), 2537.

$C_{19}H_{19}O_3Cl_4Fe$ 7-Methoxy-4-*p*-anisyl-2:3-dimethylbenzopyrylium ferrichloride (HEILBRON and ZAKI), 1905.

$C_{19}H_{19}O_5Cl_4Fe$ 7-Hydroxy-3:3′:4′-trimethoxy-5-methylflavylium ferrichloride (Robertson and Robinson), 1955.

Tetramethoxyflavylium ferrichlorides (Robertson and Robinson), 1957.

$C_{19}H_{21}O_4NCu$ Quinolino-cupric acetylacetone (Morgan and Smith), 919.

19 V

$C_{19}H_{13}O_2NI_2S$ 3:6-Di-iodo-9-toluene-*p*-sulphonylcarbazole (Tucker), 551.

$C_{19}H_{14}OCl_2BrP$ *p*-Bromotriphenylmethoxyphosphorus dichloride (Boyd and Smith), 2328.

$C_{19}H_{14}O_3NCl_2P$ *p*-Nitrotriphenylmethoxyphosphorus dichloride (Boyd and Smith), 2332.

$C_{19}H_{16}ONSbSe$ Triphenylstibine hydroxyselenocyanate (Challenger, Peters, and Halévy), 1653.

C_{20} Group.

$C_{20}H_{13}Br$ 10-Bromo-9-phenylanthracene (Cook), 2168.

$C_{20}H_{14}O_6$ α-Furoylpiperonylcarbinyl benzoate (Greene), 335.

α-Furylcarbinylpiperonoyl benzoate (Greene), 335.

$C_{20}H_{16}O_7$ 3:7-Diacetoxy-4′-methoxyflavone (Heap and Robinson), 2339.

5-Hydroxy-7:4′-diacetoxy-2-methyl*iso*flavone (Baker and Robinson), 2717.

$C_{20}H_{18}O_7$ 7-Acetoxy-3:3′:4′-trimethoxyflavone (Allan and Robinson), 2335.

$C_{20}H_{20}O_5$ 2′:3′:5:6-Tetramethoxy-2-benzylidene-1-hydrindone (Perkin, Rây, and Robinson), 953.

$C_{20}H_{22}O_2$ Ethyl dibenzylacetoacetate, reduction of (Hill), 956.

$C_{20}H_{22}O_7$ 3:4:5-Trimethoxyphenyl 2-hydroxy-4:6-dimethoxystyryl ketone (Gatewood and Robinson), 1963.

$C_{20}H_{14}O_5$ Opianylidene-*dl*-piperitone, and its calcium salt (Earl and Read), 2076.

$C_{20}H_{28}Sn$ Dibenzylethylbutylstannane (Law), 3243.

20 III

$C_{20}H_9O_8N_5$ Quinoxaline derivative of 2:4:7-trinitrophenanthraquinone (Christie and Kenner), 473.

$C_{20}H_{10}O_8N_6$ Quinoxaline derivative of tetranitrobenzil (Christie and Kenner), 475.

$C_{20}H_{13}O_3N$ Anilinohydroxy-4:9-anthraquinone (Green), 1433.

$C_{20}H_{12}O_4N_2$ 2:2′-Dinitronaphthylamine (Hodgson and Kilner), 8.

$C_{20}H_{14}OS$ 1-β-Naphthylthiol-2-naphthol (Brooker and Smiles), 1728.

$C_{20}H_{14}OS_2$ 2-Benzoyl-2-phenyl-1:3-benzdithiole (Hurtley and Smiles), 2267.

$C_{20}H_{14}O_2N_2$ Phthalylbenzidine, and its sulphate (Le Fèvre and Turner), 2482.

$C_{20}H_{14}O_6Cu$ Cupribenzoylpyruvic acid, strychnine salt (Mills and Gotts), 3130.

$C_{20}H_{14}O_6Zn$ Zincibenzoylpyruvic acid, brucine salt (Mills and Gotts), 3131.

$C_{20}H_{14}N_2S$ Benzylidenethiocarbonylbenzidine (Le Fèvre and Turner), 2483.

$C_{20}H_{15}O_4Br$ 7-Methoxy-3-(6′-bromohomopiperonyl)-2-methyl-1:4-benzopyrone (Baker), 1076.

$C_{20}H_{15}N_4Br_3$ ω-Benzylidenehydrazinobenzaldehyde-2:4-dibromophenylhydrazone (Chattaway and Parkes), 115.

$C_{20}H_{17}O_3N_3$ *N*-Acetyl-*N*′-*o*-nitrophenylbenzidine (Tucker), 3035.

$C_{20}H_{17}O_6Be$ Berylliobenzoylpyruvic acid, salts of (Mills and Gotts), 3126.

$C_{20}H_{18}ON_4$ Benzylidene δ-diphenylaminosemicarbazide (Baird and Wilson), 2375.

$C_{20}H_{19}ON$ 9-Benzoyl-6-methyltetrahydrocarbazole (Manjunath and Plant), 2263.

$C_{20}H_{19}O_3P$ Diphenyl-*p*-tolylmethylphosphinic acid, and its potassium salt (Boyd and Smith), 2333.

$C_{20}H_{19}O_4N$ Anhydrodihydroprotopine (HAWORTH and PERKIN), 1782.
2:3-Methylenedioxy-11:12-dimethoxy-6:17- or -6:15-dihydroparaberine, and it salts (CAMPBELL, HAWORTH, and PERKIN), 42.
$C_{20}H_{19}O_4P$ *m*-Methoxytriphenylmethylphosphinic acid (BOYD and SMITH), 2330.
$C_{20}H_{19}O_5N$ Anhydrodihydroprotopine oxide (HAWORTH and PERKIN), 1782.
$C_{20}H_{19}O_6N$ *N*-β-Veratrylethylmethylenedioxyhomophthalimides (HAWORTH and PERKIN), 1776.
$C_{20}H_{19}O_7N$ Methyl *N*-β-piperonylethyl-3:4-methylenedioxyhomophthalamate (HAWORTH and PERKIN), 1780.
$C_{20}H_{21}O_4N$ *dl*-Dicentrine, resolution of (HAWORTH, PERKIN, and RANKIN), 29.
2:3-Methylenedioxy-11:12-dimethoxy-6:15:16:17-tetrahydroparaberine, and its salts (CAMPBELL, HAWORTH, and PERKIN), 41.
$C_{20}H_{21}O_6N_3$ Piperidine 3:4′-dinitrophenylcinnamates (HARRISON and WOOD), 580.
$C_{20}H_{21}O_7N$ *N*-β-Veratrylethyl-3:4-methylenedioxyhomophthalamic acid (HAWORTH and PERKIN), 1776.
$C_{20}H_{21}O_8N_3$ Anhydrocotarnine-2:4-dinitro-3-methoxytoluene, and its hydrochloride (ROBINSON and WEST), 1986.
$C_{20}H_{23}O_3N$ 6:7-Dimethoxy-1-(β-dimethylaminoethyl)phenanthrene, and its hydrochloride (ROBINSON and SHINODA), 1994.
$C_{20}H_{23}O_6N_3$ Anhydrocotarnine-2-nitro-4-amino-3-methoxytoluene (ROBINSON and SHINODA), 1991.
$C_{20}H_{22}O_7N_3$ Anhydrolaudaline-2:4-dinitro-3-methoxytoluene, and its hydrochloride (ROBINSON and SHINODA), 1990.
$C_{20}H_{24}O_2N_2$ Acetyl derivative of condensation product from β-phenylhydroxylamine and acetone (BANFIELD and KENYON), 1621.
$C_{20}H_{25}O_5N_3$ Anhydrolaudaline-2-nitro-4-amino-3-methoxytoluene (ROBINSON and SHINODA), 1990.
$C_{20}H_{28}O_2N_4$ Diacetylaminotetramethylbenzidines (BELL and KENYON), 2711.
$C_{20}H_{26}BrAs$ *cyclo*Hexylphenylbenzylmethylarsonium bromide (ROBERTS, TURNER, and BURY), 1447.
$C_{20}H_{27}O_2N$ Methyldihydrothebainonemethine (CAHN), 2569.
$C_{20}H_{27}O_2N_3$ Anhydrolaudaline-2:4-diamino-3-methoxytoluene, and its dihydrochloride (ROBINSON and SHINODA), 1990.
$C_{20}H_{29}O_2N$ Dihydromethyldihydrothebainonemethine (CAHN), 2570.
$C_{20}H_{30}O_2N_4$ Methyldihydrothebainonemethine semicarbazone ($+H_2O$) (CAHN), 2569.
$C_{20}H_{32}IAs$ Di*cyclo*hexylphenylarsine ethiodide (ROBERTS, TURNER, and BURY), 1446.
$C_{20}H_{36}O_2N_6$ Trimethyl*bicyclo*hexyl-5:5′-dione disemicarbazone (BAKER), 669.

20 IV

$C_{20}H_{11}NCl_4S_2$ Bis-2:5-dichlorophenylthiolphenylacetonitrile (BROOKER and SMILES), 1726.
$C_{20}H_{13}NClAs$ Chlorodihydrodibenzphenarsazines (BURTON and GIBSON), 462.
$C_{20}H_{14}ON_2S$ Salicylidenethiocarbonylbenzidine (LE FÈVRE and TURNER), 2483.
$C_{20}H_{15}O_2N_3Br_2$ ω-*p*-Nitrobenzylidenehydrazinobenzaldehyde-2:4-dibromophenylhydrazone (CHATTAWAY and PARKES), 115.
$C_{20}H_{16}O_4N_2S_2$ 1:4-Di-*p*-toluenesulphonyl-2:5-dimethylpiperazines (KIPPING and POPE), 1078.
$C_{20}H_{17}OCl_2P$ Diphenyl-*p*-tolylmethoxyphosphorus dichloride (BOYD, SMITH, and TULLY), 2332.
$C_{20}H_{17}O_3Cl_2P$ Diphenylanisylmethoxyphosphorus dichlorides (BOYD and SMITH), 2329.

$C_{20}H_{19}O_2NS$ *p*-Toluenesulphonyl derivative of 4-methylaminodiphenyl (BELL, KENYON, and ROBINSON), 1245.

$C_{20}H_{19}O_3N_2Cl$ Substance, from phosphoryl chloride and 4-chloro-2:6′-diacetylamino-3′:4′-dimethoxystilbene (ASHLEY), 2807.

$C_{20}H_{19}O_5Cl_4Fe$ 2:3[5:6-Dimethoxyindeno(1:2)]dimethoxybenzopyrylium ferrichlorides (PERKIN, RÂY, and ROBINSON), 952.

$C_{20}H_{20}O_4NCl$ *iso*Dihydroprotopine chlorides (HAWORTH and PERKIN), 1781.

$C_{20}H_{21}O_4N_2Cl$ 4-Chloro-2:6′-diacetylamino-3′:4′-dimethoxystilbene (ASHLEY), 2806.

$C_{20}H_{21}O_6Cl_4Fe$ 5:7:3′:4′:5′-Pentamethoxyflavylium ferrichloride (GATEWOOD and ROBINSON), 1964.

$C_{20}H_{22}O_6NCl$ 7-Methoxy-4-*p*-dimethylaminophenyl-2:3-dimethylbenzopyrylium perchlorate (HEILBRON and ZAKI), 1906.

$C_{20}H_{28}O_3NI$ Methyldihydrothebainonemethine hydriodide (CAHN), 2569.

$C_{20}H_{30}O_3NI$ Methyldeoxytetrahydro-α-methylmorphimethine hydriodide (CAHN), 2566.

$C_{20}H_{30}O_3NI$ Dihydromethyldihydrothebainonemethine hydriodide (CAHN), 2570.

$C_{20}H_{33}O_3NI$ Dihydrodeoxytetrahydro-α-methylmorphimethine methiodide (CAHN), 2567.

Methyldihydrodeoxytetrahydro-α-methylmorphimethine hydriodide (CAHN), 2571.

20 V

$C_{20}H_{33}O_6NS_2As_2$ Disilver dithiolcamphor argentinitrate (DRUMMOND and GIBSON), 3076.

C_{21} Group.

$C_{21}H_{12}O_6$ 2-Benzoylanthrapurpurin (GREEN), 2201.

$C_{21}H_{13}Br_3$ 10-Bromo-9-benzylanthracene tetrabromide (COOK), 2167.

$C_{21}H_{14}O_2$ Substance, from benzylideneanthrone dibromide and silver oxide (COOK), 2171.

$C_{21}H_{15}Cl$ 10-Chloro-9-benzylanthracene (COOK), 2168.

$C_{21}H_{15}Br$ 10-Bromo-9-benzylanthracene (COOK), 2166.

$C_{21}H_{17}N$ Dihydroanthraphenone ketimine (COOK), 1682.

$C_{21}H_{18}O$ *d*- and *l*-Benzyldeoxybenzoin (MCKENZIE, ROGER, and WILLS), 788.

$C_{21}H_{18}O_7$ 5:7-Diacetoxy-4′-methoxy-2-methyl*iso*flavone (BAKER and ROBINSON), 2717.

$C_{21}H_{18}O_9$ Triacetyl-ω-benzoyloxyphloracetophenone (HEAP and ROBINSON), 2340.

$C_{21}H_{23}N_3$ *p*-Dimethylamino-*p′p″*-diaminotriphenylmethane (DUTT), 1175.

21 III

$C_{21}H_{11}N_2Cl_3$ 1:3:4-Trichloro-2-methylbenzophenanthrazine (DAVIES and LEEPER), 1419.

$C_{21}H_{12}N_2Cl_4$ 1:3-Dichloro-2-methylbenzophenanthrazine (DAVIES and LEEPER), 1416.

$C_{21}H_{13}OCl$ 10-Chloroanthraphenone (COOK), 1286.

$C_{21}H_{13}OBr$ 10-Bromoanthraphenone (COOK), 1285.

$C_{21}H_{14}OCl_2$ 9:10-Dichloro-9:10-dihydroanthraphenone (COOK), 1286.

$C_{21}H_{14}O_5N_2$ 9:10-Dinitro-9:10-dihydroanthraphenone (COOK), 1286.

$C_{21}H_{15}O_2N$ 10-Nitro-9-benzylanthracene (COOK), 2169.

$C_{21}H_{15}O_3N$ *p*-Toluidinohydroxyanthraquinone (GREEN), 1434.

$C_{21}H_{15}O_4Cl$ 3:4′:6-Trihydroxy-9-styrylxanthylium chloride ($+H_2O$) (ATKINSON and HEILBRON), 682.

$C_{21}H_{16}ON_2$ 3-Benzoylamino-2-phenylindole (ROBINSON and THORNLEY), 3145.

$C_{21}H_{17}ON$ Dihydroanthraphenone oxime (COOK), 1682.

$C_{21}H_{17}O_3N$ 9-Hydroxy-10-nitro-9-benzyl-9:10-dihydroanthracene (Cook), 2168.
$C_{21}H_{18}O_3N_2$ Benzoylaminoacetylaminodiphenyls (Bell and Kenyon), 2709.
$C_{21}H_{18}O_3N_2$ *o*-Benzoylmethylaminophenylurethane (Clark), 235.
$C_{21}H_{18}O_6N_4$ Trinitrotribenzylamine (Goss, Ingold, and Wilson), 2457.
$C_{21}H_{19}ON$ Benzoyl-2-methyl-1:2:3:4-tetrahydro-α-naphthaquinoline (Gibson, Hariharan, Menon, and Simonsen), 2252.
$C_{21}H_{19}ON_3$ ω-Benzoylaminoacetophenone phenylhydrazone (Robinson and Thornley), 3145.
$C_{21}H_{19}NS$ Thiobenzoyldi-*p*-tolylamine (Chapman), 2298.
N-*p*-Tolylbenzimino-*p*-tolyl thioether (Chapman), 2298.
$C_{21}H_{20}ON_4$ Acetophenone-δ-diphenylaminosemicarbazone (Baird and Wilson), 2375.
$C_{21}H_{20}O_4N_2$ Tetra-acetyl-2:7-diaminofluorene (Morgan and Thomason), 2695.
$C_{21}H_{22}O_4N_2$ 6:7-Dimethoxy-1-(3′:4′-methylenedioxy-ω-cyanobenzyl)-2-methyltetrahydro*iso*quinoline (Edwards), 744.
$C_{21}H_{23}O_5N$ Anhydrodihydrocryptopine oxide, and its hydrochloride (Haworth and Perkin), 1779.
Anhydrotetrahydromethylberberine oxide, and its hydrochloride (Haworth and Perkin), 449.
$C_{21}H_{23}O_7N$ Methyl *N*-β-veratrylethyl-3:4-methylenedioxyhomophthalamate (Haworth and Perkin), 1776.
$C_{21}H_{23}O_9N_3$ Anhydrocotarnine-2:6-dinitrohomoveratrole (Graesser-Thomas, Gulland, and Robinson), 1976.
$C_{21}H_{25}O_6N_2$ Ethyl 4-(*m*-nitro-*p*-dimethylaminophenyl)-2:6-dimethylpyridine-3:5-dicarboxylate (Hinkel and Madel), 163.
$C_{21}H_{27}O_4N_3$ Ethyl 4-(*m*-nitro-*p*-dimethylaminophenyl)-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylate (Hinkel and Madel), 163.
$C_{21}H_{32}O_3N_4$ Dihydromethyldihydrothebainonemethine semicarbazone (Cahn), 2570.
$C_{21}H_{40}O_2Cl_2$ β-Stearyl dichlorohydrin (Whitby), 1460.

21 IV

$C_{21}H_{18}O_2N_2Ni$ Nickel ethylenediaminobisacetylacetone (Morgan and Smith), 920.
$C_{21}H_{23}O_4N_2Br$ Ethyl 4-(*m*-bromo-*p*-dimethylaminophenyl)-2:6-dimethylpyridine-3:5-dicarboxylate (Hinkel and Madel), 163.
$C_{21}H_{28}O_4NI$ Acetylneopine methiodide (van Duin, Robinson, and Smith), 906.
$C_{21}H_{27}O_4N_2Br$ Ethyl 4-(*m*-bromo-*p*-dimethylaminophenyl)-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylate (Hinkel and Madel), 162.
$C_{21}H_{27}O_6NS$ *isoapo*Morphine dimethyl ether methosulphate (Robinson and Shinoda), 1994.

21 V

$C_{21}H_{11}ONCl_4S_2$ 5:7-Bis-2′:5′-dichlorophenylthiol-8-hydroxyquinoline (Brooker and Smiles), 1729.

C_{22} Group.

$C_{22}H_{18}O_4$ Methoxybenzoylbenzoins (Greene), 328.
Triacetyl-2-methylgenistein (Baker and Robinson), 2717.
$C_{22}H_{18}O_9$ Triacetylkaempferide (Heap and Robinson), 2341.
$C_{22}H_{20}O_9$ 5:7-Diacetoxy-3:3′:4′-trimethoxyflavone (Allan and Robinson), 2336.
$C_{22}H_{22}O_{11}$ *p*-Ethylcarbonato-*m*-methoxybenzoic anhydride (Heap and Robinson), 2344.

$C_{22}H_{33}N$ *apo*Conessine, and its salts (KANGA, AYYAR, and SIMONSEN), 2125.
$C_{22}H_{42}O_3$ 10-Ketobehenic acid (G. M. and R. ROBINSON), 2208.

22 III

$C_{22}H_{15}O_3Cl$ 3′:4′-Methylenedioxy-9-styrylxanthylium chloride, and its zinc chloride double salt (ATKINSON and HEILBRON), 682.
$C_{22}H_{15}O_5Cl$ 3:6-Dihydroxy-4′:5′-methylenedioxy-9-styrylxanthylium chloride (ATKINSON and HEILBRON), 683.
$C_{22}H_{17}O_2Cl$ 4′-Methoxy-9-styrylxanthylium chloride, and its ferrichloride (ATKINSON and HEILBRON), 681.
$C_{22}H_{17}O_3Cl$ 4′-Hydroxy-3′-methoxy-9-styrylxanthylium chloride (ATKINSON and HEILBRON), 682.
$C_{22}H_{17}O_4Cl$ 3:6-Dihydroxy-4′-methoxy-9-styrylxanthylium chloride (+ H_2O) (ATKINSON and HEILBRON), 683.
4′-Hydroxy-9-styrylxanthylium chloride (ATKINSON and HEILBRON), 680.
$C_{22}H_{17}O_5Cl$ 3:4′:6-Trihydroxy-5′-methoxy-9-styrylxanthylium chloride (ATKINSON and HEILBRON), 683.
$C_{22}H_{18}O_4N_4$ 1-Hydroxy-3-(4′-nitrophenyl)-1:3-dihydrophthalazine-4-acetanilide (ROWE, LEVIN, BURNS, DAVIES, and TEPPER), 702.
$C_{22}H_{18}NS_2$ Di-*p*-tolylthiolphenylacetonitrile (BROOKER and SMILES), 1726.
$C_{22}H_{22}ON_4$ Dibenzyl ketone δ-anilinosemicarbazone (BAIRD and WILSON), 2373.
$C_{22}H_{23}O_7N_4$ Dibenzyldimethylammonium picrate (GOSS, INGOLD, and WILSON), 2462.
$C_{22}H_{23}O_6N$ Narcotine oxide (DRUMMOND and MCMILLAN), 2704.
$C_{22}H_{23}O_9Cl$ 4′-β-Glucosidoxy-7-hydroxy-3-methoxyflavylium chloride (+ $\frac{1}{2}H_2O$) (ROBERTSON and ROBINSON), 1717.
$C_{22}H_{25}O_7N_3$ Anhydrocotarnine-2-nitro-4-acetylamino-3-methoxytoluene (ROBINSON and SHINODA), 1992.
$C_{22}H_{25}O_9N$ Hydroxy-acid, and its salts, from narcotine oxide (DRUMMOND and MCMILLAN), 2704.
$C_{22}H_{26}O_4N_4$ 4:4′-Dipiperidino-3:5′-dinitrodiphenyl (LE FÈVRE and TURNER), 1764.
$C_{22}H_{27}O_6N_3$ Anhydrolaudaline-2-nitro-4-acetylamino-3-methoxytoluene (ROBINSON and SHINODA), 1991.
$C_{22}H_{29}O_4N_3$ Anhydrolaudaline-2-amino-4-acetylamino-3-methoxytoluene (+ H_2O) (ROBINSON and SHINODA), 1993.
$C_{22}H_{31}O_2N$ Cubebol phenylurethane (HENDERSON and ROBERTSON), 2815.

22 IV

$C_{22}H_{12}OCl_4S_2$ 2:4-Bis-2′:5′-dichlorophenylthiol-1-naphthol (BROOKER and SMILES), 1728.
$C_{22}H_{16}O_2Cl_4S_2$ Ethyl bis-2:5-dichlorophenylthiolphenylacetate (BROOKER and SMILES), 1726.
$C_{22}H_{31}O_2NBr_2$ Cubebol phenylurethane dibromide (HENDERSON and ROBERTSON), 2815.

C_{23} Group.

$C_{23}H_{16}O_3$ Acetate of substance $C_{21}H_{14}O_2$ (COOK), 2171.
$C_{23}H_{18}O_2$ 9-Benzylanthranyl 10-acetate (COOK), 2165.
Dihydroanthraphenone acetate (COOK), 1682.
$C_{23}H_{24}N_2$ *leuco*-3:6-Tetramethyldiamino-9-phenylfluorene (DUTT), 1181.
$C_{23}H_{27}N_3$ Substance, from α-picoline and Michler's hydrol (HUMPHRIES), 375.
$C_{23}H_{28}O_{12}$ *p*-Tetra-acetyl-β-glucosidoxy-ω-methoxyacetophenone (ROBERTSON and ROBINSON), 1716.

$C_{23}H_{34}O_{11}$ Ethyl ω-1:2:4-tricarbethoxy-2-keto-*cyclo*pentylmethylsuccinates (INGOLD and SHOPPEE), 1916.

23 III

$C_{23}H_{18}O_2N_2$ 3-Methoxy-2-ethoxyphenanthraphenazine (ALLAN and ROBINSON), 379.

$C_{23}H_{19}O_3P$ Diphenylnaphthylmethylphosphinic acids, and their salts (BOYD and SMITH), 2331.

$C_{23}H_{19}O_4N$ 4-Acetylbenzoylamino-4′-acetoxydiphenyl (BELL and KENYON), 2713.

$C_{23}H_{21}ON$ Benzoyl-2-methyl-1:2:3:4-tetrahydroacenaphthpyridine (NAIR and SIMONSEN), 3142.

$C_{23}H_{21}O_3N_3$ *p*-Nitrobenzylideneacetyl*iso*propylidenebenzidine (DENNETT and TURNER), 481.

$C_{23}H_{23}O_9Cl$ 4′-β-Glucosidoxy-7-hydroxy-3-methoxy-5-methylflavylium chloride (+ $1\frac{1}{2}H_2O$) (ROBERTSON and ROBINSON), 1719.

$C_{23}H_{27}O_5N_3$ Anhydrocotarnine-2:4-diacetylaminotoluene (ROBINSON and WEST), 1935.

23 IV

$C_{23}H_{17}OCl_2P$ Diphenylnaphthylmethoxyphosphorus dichlorides (BOYD and SMITH), 2330.

$C_{23}H_{15}ONS_2$ 5:7-Di-*p*-tolylthiol-8-hydroxyquinoline (BROOKER and SMILES), 1729.

$C_{23}H_{20}O_3NCl$ 3:6-Dihydroxy-4′-dimethylamino-9-styrylxanthylium chloride (+ H_2O) (ATKINSON and HEILBRON), 683.

$C_{23}H_{23}O_4N_2I$ Dehydro-anhydrolaudaline-4-acetylamino-3-methoxytoluene methiodide (ROBINSON and SHINODA), 1994.

C_{24} Group.

$C_{24}H_{12}N_6$ Phenazineazineazine (DUTT), 1180.

$C_{24}H_{16}N_2$ 3:3′-Dicarbazyl (TUCKER), 3037.

$C_{24}H_{16}N_6$ 4:4′-Di-1″:2″:3″-benztriazolyldiphenyl (TUCKER), 3036.

$C_{24}H_{12}O_5$ 5:7-Dihydroxy-4′-methoxy-2-styryl*iso*flavone (BAKER and ROBINSON), 2718.

$C_{24}H_{19}N_7$ Benzeneazobenzeneazobenzeneazoaniline (DUTT), 1177.

$C_{24}H_{20}O_2$ 1-α-Naphthyl-2:2-diphenylethylene glycol (MCKENZIE and DENNLER), 1601.

$C_{24}H_{20}O_{11}$ Tetra-acetyl*iso*rhamnetin (HEAP and ROBINSON), 2343.

$C_{24}H_{22}N_4$ *NN′*-Di-*o*-aminophenylbenzidine, and its dihydrochloride (TUCKER), 3036.

$C_{24}H_{34}O_{16}$ Hepta-acetyl methylmaltoside (IRVINE and BLACK), 874.

$C_{24}H_{38}O_{11}$ Heptamethyl methylmaltoside (IRVINE and BLACK), 870.

$C_{24}H_{40}N_2$ Conessine (KANGA, AYYAR, and SIMONSEN), 2123.

24 III

$C_{24}H_{16}O_6N_2$ 3:3′-Dinitro-4:4′-diphenoxydiphenyl (LE FÈVRE and TURNER), 2048.

$C_{24}H_{13}ON_6$ Benzeneazobenzeneazobenzeneazophenol (DUTT), 1177.

$C_{24}H_{18}O_2Te_2$ *pp′*-Diphenoxydiphenyl ditelluride (DREW), 228.

$C_{24}H_{16}O_4N_4$ 3:3′-Dinitro-4:4′-dianilinodiphenyl (LE FÈVRE and TURNER), 2048.
Di-*o*-nitrophenylbenzidine (TUCKER), 3034.

$C_{24}H_{18}O_2Te_2$ Phenoxtellurone (DREW), 3069.

$C_{24}H_{18}O_6N_2$ Di-ω-6-nitropiperonyl*iso*butyrophenone (PERKIN, RAY, and ROBINSON), 947.

$C_{24}H_{12}N_2As_2$ 10:10′-Bis-5:10-dihydrophenarsazine (BURTON and GIBSON), 2246.

$C_{24}H_{20}ON_2$ β-1-Naphthylaminocrotono-1-naphthylamide (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2253.

$C_{24}H_{23}O_3N$ Triacetyl derivative of dihydroxydihydrocodeine (CAHN and ROBINSON), 910.

24 IV

$C_{24}H_{12}O_2Cl_6S_2$ 2:4:6-Tri-2′:5′-dichlorophenylthiolresorcinol (BROOKER and SMILES), 1728.

$C_{24}H_{15}O_2Cl_3S_3$ 2:4:6-Tri-*p*-chlorophenylthiolresorcinol (BROOKER and SMILES), 1728.

$C_{24}H_{15}O_2Cl_3S_3$ 2:4:6-Tri-*p*-chlorophenylthiolphloroglucinol (BROOKER and SMILES), 1727.

$C_{24}H_{16}O_2Cl_2S_2$ 2:4-Di-4′-chlorophenylthiol-1-naphthol (BROOKER and SMILES), 1728.

$C_{24}H_{16}O_4N_4S_2$ Substance, from diaminothianthren and resorcinol (SEN and RÂY), 1141.

$C_{24}H_{16}O_{10}S_2Te_2$ Phenoxtellurine sulphate (DREW), 3070.

$C_{24}H_{18}O_2Cl_2Te$ *pp′*-Diphenoxydiphenyltelluridichloride (DREW), 227.

$C_{24}H_{18}O_6N_6S_4$ Thianthren-2:6-bisdiazoaminobenzene-4′-sulphonic acid (SEN and RÂY), 1141.

$C_{24}H_{20}O_4N_2S_2$ 1-Acetylaminonaphthyl 4-disulphoxide (CHILD and SMILES), 2701.

$C_{24}H_{20}O_8STe_2$ Diphenoxtellurylium hydroxybisulphate hydrate (DREW), 3067.

$C_{24}H_{22}O_{12}S_2Te_2$ Diphenoxtellurylium dibisulphate dihydrate (DREW), 3069.

$C_{24}H_{24}O_{13}S_2Te_2$ Diphenoxtellurylium dibisulphate trihydrate (DREW), 3068.

$C_{24}H_{28}O_{21}S_4Te_2$ Diphenoxtellurylium dibisulphate disulphuric acid trihydrate (DREW), 3067.

$C_{24}H_{33}O_4N_2I$ Bis-*p*-dimethylaminobenzylidene pentaerythritol methiodide (FAIRBOURNE and WOODLEY), 3241.

24 V

$C_{24}H_{22}O_4N_4S_2As_2$ 3′-Aminobenzenesulphonyl-4-aminoarsenobenzene (HEWITT, KING, and MURCH), 1364.

C_{25} Group.

$C_{25}H_{18}O$ Di-*p*-naphthylvinyl ketone (GIBSON, HARIHARAN, MENON, and SIMONSEN), 2257.

$C_{25}H_{21}N_3$ 4-Diazomethylaminodiphenyl (BELL, KENYON, and ROBINSON), 1246.

$C_{25}H_{22}N_4$ *p*-Benzeneazo-*p′p″*-diaminotriphenylmethane (DUTT), 1175.

25 III

$C_{25}H_{20}ON_2$ *s*-Di-5-acenaphthylcarbamide (NAIR and SIMONSEN), 3143.

$C_{25}H_{21}O_7Cl$ 7-Methoxy-4-phenyl-2-*p*-hydroxystyryl-3-methylbenzopyrylium perchlorate (HEILBRON and ZAKI), 1904.

$C_{25}H_{22}ON_4$ Carbonylbenzidine, and its sulphate (LE FÈVRE and TURNER), 2483.
p-4-Hydroxybenzeneazo-*pp″*-diaminotriphenylmethane (DUTT), 1176.

$C_{25}H_{26}O_2N_2$ 3:6-Tetramethyldiamino-9-phenylfluorene acetate (DUTT), 1182.

$C_{25}H_{26}O_3N_2$ Benzoyl derivative of condensation product of β-phenylhydroxylamine and acetone (BANFIELD and KENYON), 1622.

$C_{25}H_{40}BrAs$ Tri*cyclo*hexylarsine benzobromide (ROBERTS, TURNER, and BURY), 1446.

25 IV

$C_{25}H_{30}O_4N_{24}Cu_5$ Substance from cuprous cyanide, hydrocyanic acid, and ethylenediamine (MORGAN and BURSTALL), 2025.

C_{26} Group.

$C_{26}H_{16}$ Bisdiphenylene-ethylene, absorption spectrum of (CAPPER and MARSH), 725.

$C_{26}H_{20}$ 9:10-Diphenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3084.

26 II

$C_{26}H_{16}Cl_2$ 9:10-Di-*p*-chlorophenylanthracene (INGOLD and MARSHALL), 3085.

$C_{26}H_{16}Br_2$ 9:10-Di-*p*-bromophenylanthracene (INGOLD and MARSHALL), 3086.

$C_{26}H_{17}Cl$ 2-Chloro-9:10-diphenylanthracene (INGOLD and MARSHALL), 3087.

$C_{26}H_{17}Br$ 2-Bromo-9:10-diphenylanthracene (INGOLD and MARSHALL), 3087.

$C_{26}H_{18}N_2$ Quinoxaline derivative of 3:4-diaminodiphenyl (BELL and KENYON), 2708.

$C_{26}H_{18}Cl_2$ 9:10-Di-*p*-chlorophenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3086.

$C_{26}H_{18}K_2$ 9:10-Dipotassio-9:10-diphenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3084.

$C_{26}H_{18}Na_2$ 9:10-Disodio-9:10-diphenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3084.

$C_{26}H_{22}O$ Substance, from dehydration of 1-α-naphthyl-2:2-dibenzylethylene glycol (MCKENZIE and DENNLER), 1602.

$C_{26}H_{23}N_7$ Benzeneazobenzeneazobenzeneazodimethylaniline (DUTT), 1177.

$C_{26}H_{26}O_2$ 1-α-Naphthyl-2:2-dibenzylethylene glycol (MCKENZIE and DENNLER), 1601.

$C_{26}H_{42}O_6$ Bornyl dimethoxysuccinates (PATTERSON, FULTON, and SEMPLE), 3225.

$C_{26}H_{52}O$ Ketone, from oxidation of paraffin wax (FRANCIS and GAUNTLETT), 2381.

$C_{26}H_{54}O$ Alcohol, from oxidation of paraffin wax (FRANCIS and GAUNTLETT), 2381.

26 III

$C_{26}H_{16}Cl_2Br_2$ 9:10-Dichloro-9:10-di-*p*-bromophenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3088.

$C_{26}H_{18}OS_4$ 2-Phenyl-1:3-benzdithiole 2-oxide (HURTLEY and SMILES), 1827.

$C_{26}H_{18}O_2N_2$ Dianilinoanthraquinone (GREEN), 1433.

$C_{26}H_{18}O_2Cl_2$ 9:10-Dihydroxy-9:10-di-*p*-chlorophenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3085.

$C_{26}H_{18}O_2Br_2$ 9:10-Dihydroxy-9:10-di-*p*-bromophenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3086.

$C_{26}H_{19}O_2Cl$ 2-Chloro-9:10-dihydroxy-9:10-diphenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3087.

$C_{26}H_{19}O_2Br$ 2-Bromo-9:10-dihydroxy-9:10-diphenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3087.

$C_{26}H_{19}O_3N_3$ *p*-Nitrobenzylidenesalicylidenebenzidine (DENNETT and TURNER), 481.

$C_{26}H_{20}O_2N_2$ 3:4-Dibenzoyldiaminodiphenyl (BELL and KENYON), 2708.
Disalicylidene-3:5-diaminodiphenyl (DENNETT and TURNER), 481.

$C_{26}H_{20}NBr$ 9-Benzylanthranyl-10-pyridinium bromide (COOK), 2167.

$C_{26}H_{20}N_6Br_4$ Hydrazobenzaldehyde-2:4-dibromophenylhydrazone (CHATTAWAY and PARKES), 116.

$C_{26}H_{21}O_5P$ *m*-Benzoyloxytriphenylmethylphosphinic acid, and its salts (BOYD and SMITH), 2330.

$C_{26}H_{22}O_4N_4$ 3:3′-Dinitro-4:4′-dimethylanilinodiphenyl (LE FÈVRE and TURNER), 2048.

$C_{26}H_{23}O_6N$ Benzoyl-6:7-methylenedioxy-3-(3′:4′-dimethoxybenzoyl)-1:2:3:4-tetrahydro*iso*quinoline (CAMPBELL, HAWORTH, and PERKIN), 39.

$C_{26}H_{33}O_2N$ Cubebol α-naphthylurethane (HENDERSON and ROBERTSON), 2815.

$C_{26}H_{32}O_3N_2$ Substance, from anhydrolaudaline-2-nitro-4-amino-3-methoxytoluene and acetic anhydride (ROBINSON and SHINODA), 1991.

26 IV

$C_{26}H_{16}OCl_4S_2$ Phenyl αα-bis-2:5-dichlorophenylthiolbenzyl ketone (BROOKER and SMILES), 1727.

$C_{26}H_{18}O_2N_2Br_2$ Disalicylidene-4:4′-dibromo-2:3′-diaminodiphenyl (DENNETT and TURNER), 479.

$C_{26}H_{20}N_4Br_8S$ 3:5-Diphenylimino-2:4-diphenyltetrahydro-1:2:4-thiodiazole octabromide (HUNTER), 536.

$C_{26}H_{20}N_4I_6S$ 3:5-Diphenylimino-2:4-diphenyltetrahydro-1:2:4-thiodiazole hexaiodide (HUNTER), 536.

$C_{26}H_{22}O_2N_4Cl_2$ Di-Meldola's blue (DUTT), 1180.

$C_{26}H_{22}O_4N_4As_2$ 3′-Aminobenzoyl-3-amino-4-hydroxyarsenobenzene (HEWITT and KING), 828.

$C_{26}H_{22}O_6N_4As_2$ Aminohydroxybenzoylaminohydroxyarsenobenzenes (HEWITT and KING), 827.

$C_{26}H_{23}O_3Cl_4Fe$ 7-Methoxy-4-phenyl-2-*p*-methoxystyryl-3-methylbenzopyrylium ferrichloride (HEILBRON and ZAKI), 1905.

$C_{26}H_{23}O_4Cl_4Fe$ 7-Methoxy-4-*p*-anisyl-2-*p*-hydroxystyryl-3-methylbenzopyrylium ferrichloride (HEILBRON and ZAKI), 1906.

7-Methoxy-4-phenyl-2-*p*-hydroxy-*m*-methoxystyryl-3-methylbenzopyrylium ferrichloride (HEILBRON and ZAKI), 1905.

$C_{26}H_{44}O_4N_6Cu_2$ Ethylenediamminodicupric bisethylenediaminobisacetylacetone (MORGAN and SMITH), 919.

26 V

$C_{26}H_{26}O_4N_4S_2As_2$ 3′-Aminotoluene sulphonyl-4-aminoarsenobenzene (HEWITT, KING, and MURCH), 1362.

C_{27} Group.

$C_{27}H_{18}O$ Phenylanthraphenone (COOK), 2170.

$C_{27}H_{20}O$ 10-Phenyl-9:10-dihydroanthraphenone (COOK), 2171.

$C_{27}H_{27}N_5$ *p*-4-Dimethylaminobenzeneazo-*p′p″*-diaminotriphenylmethane (DUTT), 1175.

$C_{27}H_{29}N_3$ Substance, from quinaldine and Michler's hydrol (HUMPHRIES), 375.

27 III

$C_{27}H_{18}O_2N_2$ Benzylidenephthalylbenzidine (LE FÈVRE and TURNER), 2482.

$C_{27}H_{18}O_3N_2$ Salicylidenephthalylbenzidine (LE FÈVRE and TURNER), 2482.

$C_{27}H_{24}O_3S_2$ 2:4:6-Tri-*p*-tolylthiolphloroglucinol (BROOKER and SMILES), 1727.

27 IV

$C_{27}H_{19}O_2Cl_3S_2$ Phenyl α-5-chloro-2-methoxyphenylthiol-α-2:5-dichlorophenylthiolbenzyl ketone (BROOKER and SMILES), 1727.

$C_{27}H_{25}O_6NCl$ 7-Methoxy-4-phenyl-2-*p*-dimethylaminostyryl-3-methylbenzopyrylium perchlorate (HEILBRON and ZAKI), 1905.

27 V

$C_{27}H_{25}O_3NCl_4Fe$ 7-Methoxy-4-phenyl-2-*p*-dimethylaminostyryl-3-methylbenzopyrylium ferrichloride (HEILBRON and ZAKI), 1905.

C_{28} Group.

$C_{28}H_{20}$ Dihydrodianthranyl (MATTHEWS), 239.

$C_{28}H_{22}$ 9:10-Di-*p*-tolylanthracene (INGOLD and MARSHALL), 3085.

28 II

$C_{28}H_{18}Br_2$ Dibromodihydrodianthranyl (MATTHEWS), 239.
$C_{28}H_{20}O$ 10-Benzylanthraphenone (COOK), 2169.
$C_{28}H_{20}O_2$ 9:10-Dibenzoyl-9:10-dihydroanthracene (COOK), 1683.
$C_{28}H_{22}O$ 10-Benzyl-9:10-dihydroanthraphenone (COOK), 2170.
$C_{28}H_{22}O_2$ 9:10-Di-*p*-anisylanthracene (INGOLD and MARSHALL), 3086.
$C_{28}H_{22}O_7$ 5:7-Diacetoxy-4′-methoxy-2-styryl*iso*flavone (BAKER and ROBINSON), 2719.
$C_{28}H_{22}K_2$ Dipotassio-9:10-di-*p*-tolylanthracene (INGOLD and MARSHALL), 3085.
$C_{28}H_{22}Na_2$ Disodio-9:10-di-*p*-tolylanthracene (INGOLD and MARSHALL), 3085.
$C_{28}H_{24}O_2$ 9:10-Dihydroxy-9:10-di-*p*-tolyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3085.
$C_{28}H_{24}O_4$ 9:10-Dihydroxy-9:10-di-*p*-anisyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3086.
$C_{28}H_{24}O_6$ 5-Acetoxy-7:4′-dimethoxy-2-styryl-6-methyl*iso*flavone (BAKER and ROBINSON), 2719.
$C_{28}H_{26}O$ *d*-αβ-Diphenyl-αβ-dibenzylethyl alcohol (MCKENZIE, ROGER, and WILLS), 790.
$C_{28}H_{30}O$ Substance, from $C_{28}H_{32}O_2$ and acetic acid (FARROW and KON), 2135.
$C_{28}H_{31}N_3$ Substance, from *p*-toluquinaldine and Michler's hydrol (HUMPHRIES), 375.
$C_{28}H_{32}O_2$ Substance, from α-Δ¹-*cyclo*hexenylacetophenone and sodium ethoxide (FARROW and KON), 2135.
$C_{28}H_{56}O$ Ketone, from oxidation of paraffin wax (FRANCIS and GAUNTLETT), 2381.
$C_{28}H_{58}O$ Alcohol, from oxidation of paraffin wax (FRANCIS and GAUNTLETT), 2381.

28 III

$C_{28}H_{19}O_3N$ Nitrohydrodianthranyl (MATTHEWS), 239.
$C_{28}H_{20}O_2N_2$ 9:9′-Diacetyl-3:3′-dicarbazyl (TUCKER), 3038.
$C_{28}H_{22}O_2N$ Di-*p*-toluidinoanthraquinone (GREEN), 1434.
$C_{28}H_{22}O_6N_4$ *NN′*-Diacetyl-*NN′*-di-*o*-nitrophenylbenzidine (TUCKER), 3035.
$C_{28}H_{24}ON_2$ β-5-Acenaphthylaminocroton-5-acenaphthylamide (NAIR and SIMONSEN), 3142.
$C_{28}H_{26}O_2S_3$ 2:4:6-Tri-*p*-tolylthiolorcinol (BROOKER and SMILES), 1728.
$C_{28}H_{42}O_2N_2$ *d*- and *l*-*cis*-2:5-Dimethylpiperazine-*d*-bismethylenecamphor (KIPPING and POPE), 1078.

28 IV

$C_{28}H_{14}O_4N_2Cl_2$ Dichlorodinitroanthranyl (MATTHEWS), 240.
$C_{28}H_{22}O_2N_2As_2$ 10:10′-Bis-5-acetyl-5:10-dihydrophenarsazine (BURTON and GIBSON), 2247.

28 V

$C_{28}H_{29}O_2NCl_4Fe$ 7-Methoxy-4-*p*-anisyl-2-*p*-dimethylaminostyryl-3-methylbenzopyrylium ferrichloride (HEILBRON and ZAKI), 1906.

C_{29} Group.

$C_{29}H_{58}O$ Ketone, from oxidation of paraffin wax (FRANCIS and GAUNTLETT), 2381.

29 III

$C_{29}H_{24}N_2I$ Substance, from *p*-toluquinaldine methiodide and Michler's hydrol (HUMPHRIES), 375.

C_{30} Group.

$C_{30}H_{50}$ Squalene, constitution of (HEILBRON, KAMM, and OWENS), 1630.
$C_{30}H_{62}$ Dodecahydrosqualene (HEILBRON, HILDITCH, and KAMM), 3135.

30 II

$C_{30}H_{22}O_9$ Benzoylvanillic anhydride (HEAP and ROBINSON), 2342.
$C_{30}H_{56}Br_6$ Squalene hexahydrobromide (HEILBRON, KAMM, and OWENS), 1641.

30 III

$C_{30}H_{23}ON_8$ Benzeneazobenzeneazobenzeneazobenzeneazophenol (DUTT), 1178.
$C_{30}H_{31}O_{13}Cl$ 4′-Tetra-acetyl-β-glucosidoxy-7-hydroxy-3-methoxyflavylium chloride (ROBERTSON and ROBINSON), 1717.
$C_{30}H_{30}O_3N_4$ Tribenzoyltriaminotripropylamine (MANN and POPE), 492.

30 IV

$C_{30}H_{18}O_6Cl_6S_2$ 2:4:6-Tri-2′:5′-dichlorophenylthiolphloroglucinol (BROOKER and SMILES), 1727.
$C_{30}H_{20}O_4N_2Cu$ Copper ω-4-nitrobenzoylacetophenone (BRADLEY and ROBINSON), 2364.
$C_{30}H_{44}O_2S_2Ni$ Nickel thiolcamphor (DRUMMOND and GIBSON), 3076.

30 V

$C_{30}H_{48}O_2Cl_4S_2Sn_2$ Thiolcamphor stannochloride (DRUMMOND and GIBSON), 3076.

C_{31} Group.

$C_{31}H_{26}N_2Br_2$ 9-Benzyl-9:10-dihydroanthraquinyl-9:10-dipyridinium dibromide (COOK), 2167.
$C_{31}H_{30}N_4S$ Bis-dibenzyl ketone thiocarbohydrazone (STEPHEN and WILSON), 2537.
$C_{31}H_{33}O_{13}Cl$ 4′-Tetra-acetyl-β-glucosidoxy-7-hydroxy-3-methoxy-5-methylflavylium chloride (+ H_2O) (ROBERTSON and ROBINSON), 1719.

C_{32} Group.

$C_{32}H_{27}N_9$ Benzeneazobenzeneazobenzeneazobenzeneazodimethylaniline (DUTT), 1178.

32 IV

$C_{32}H_{20}O_2N_4S_2$ Substance, from diazotised diaminothianthren and β-naphthol (SEN and RÂY), 1141.

C_{33} Group.

$C_{33}H_{24}O_2$ 9-Hydroxy-9-triphenylmethylanthrone (INGOLD and MARSHALL), 3087.
$C_{33}H_{24}O_6$ 5-Hydroxy-7-cinnamoyloxy-4′-methoxy-2-styryl*iso*flavone (BAKER and ROBINSON), 2718.

33 III

$C_{33}H_{30}O_6N_4$ Triphthalimidotripropylamine (MANN and POPE), 491.

33 IV

$C_{33}H_{31}O_6N_4Br$ Triphthalimidotripropylamine hydrobromide (MANN and POPE), 490.

C_{34} Group.

$C_{34}H_{18}O_{10}$ Difluorescein (DUTT), 1180.
$C_{34}H_{42}N_4$ Bistetramethyldiaminodiphenylmethane (DUTT), 1178.

34 IV

$C_{34}H_{36}O_2N_4Cl_2$ Dipyronine G (DUTT), 1179.

C_{36} Group.

$C_{36}H_{32}O_8N_2$ Pyrazine from *iso*nitroso-3:4-dimethoxyphenyl 3:4-methylenedioxy-β-phenyl ethyl ketone (CAMPBELL, HAWORTH, and PERKIN), 38.

$C_{36}H_{34}O_6Cu$ Copper *iso*propoxybenzoylacetophenone (BRADLEY and ROBINSON), 2362.

$C_{36}H_{36}O_{10}Cu$ Copper 3:4:5-trimethoxybenzoylacetophenone (BRADLEY and ROBINSON), 2366.

36 IV

$C_{36}H_{32}O_{22}S_4Te_2$ Phenoxtellurine dibisulphate (DREW), 3070.

C_{38} Group.

$C_{38}H_{30}N_2$ 9:10-Dianilino-9:10-diphenyl-9:10-dihydroanthracene (INGOLD and MARSHALL), 3083.

38 III

$C_{38}H_{46}O_4N_4$ Bistetramethyldiaminodiphenylcarbinol diacetate (DUTT), 1178.

C_{39} Group.

$C_{39}H_{30}ON_4$ Benzylidenecarbonylbenzidine (LE FÈVRE and TURNER), 2483.

$C_{39}H_{30}O_2N_4$ Salicylidenecarbonylbenzidine (LE FÈVRE and TURNER), 2483.

C_{41} Group.

$C_{41}H_{36}O_4$ Substance, from benzyl methyl ketone and salicylaldehyde (DICKINSON), 2239.

C_{42} Group.

$C_{42}H_{30}O_2$ 10:10′-Dibenzoyl-9:9′:10:10′-tetrahydro-9:9′-dianthranyl (COOK), 1680.

$C_{42}H_{42}Sn_2$ Hexabenzyldistannane (LAW), 3243.

C_{46} Group.

$C_{46}H_{34}O_4$ Dibenzoyltetrahydrodianthranyl diacetate (COOK), 1683.

$C_{46}H_{50}N_4$ *leuco*-Dimalachite-green (DUTT), 1179.

C_{50} Group.

$C_{50}H_{54}O_4N_4$ Dimalachite-green diacetate (DUTT), 1179.

ERRATA.

Vol. 115 (1919).

Page	Line	
1198	6*	*for* "0·81617" *read* "0·81417."

Vol. 127 (1925).

1998	20	*for* "2830" *read* "2839."
2814	31	*for* "2 mols. of neutralised sodium oxide to 1 mol. of silica" *read* "1 mol. of neutralised sodium oxide to 2 mols. of silica."
2816	3	*for* "0·405*N*" *read* "0·0405*N*."
3042	10*	*for* "CHO_3ClBrS" *read* "CH_2O_3ClBrS."
3045	22	*for* "$C_6H_4O_6$" *read* "$C_6H_4O_6N_2$," *and transfer the two entries to sub-group* 6 III.

Vol. (1926).

455 463 464	2* 6* 1	*for* "10-acetyl-5 : 10-dihydrophenarsazine" read "10-acetoxy-5 : 10-dihydrophenarsazine."
1032	15	*for* "Thomson" read "Thomsen."
1042	20*	The work to which reference is made in the sentence beginning "It was after his return to South Kensington . . ." was carried out at the Government Laboratory, with A. G. Francis as Sir Edward Thorpe's collaborator. The results were published in 1910.
1043	13	*for* "Government Chemists' Department" *read* "Department of the Government Chemist."
1896	14*	*for* "Hertz" *read* "Herty," *and for* "1892, 14, 107" *read* "1896, 18, 290."

* From bottom.

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